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# The HN(3) + CO(2) laser: an analytical and experimental investigation

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Monterey, California. Naval Postgraduate School

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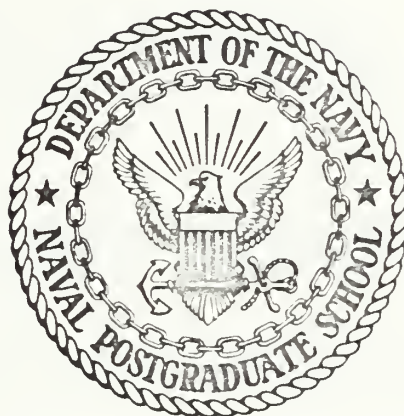
THE  $\text{HN}_3 + \text{CO}_2$  LASER:  
AN ANALYTICAL AND EXPERIMENTAL INVESTIGATION

Francis Kenneth Helmsin

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# NAVAL POSTGRADUATE SCHOOL

## Monterey, California



# THESIS

The  $\text{HN}_3 + \text{CO}_2$  Laser:

An Analytical and Experimental Investigation

by

Francis Kenneth Helmsin

Thesis Advisor:

D. J. Collins

March 1972



The  $\text{HN}_3 + \text{CO}_2$  Laser:  
An Analytical and Experimental Investigation

by

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Submitted in partial fulfillment of the  
requirements for the degree of

MASTER OF SCIENCE IN AERONAUTICAL ENGINEERING

from the  
NAVAL POSTGRADUATE SCHOOL  
March 1972



## ABSTRACT

One of the most important methods of obtaining laser action, both from a technological and scientific viewpoint, is the chemically-pumped laser. The  $\text{HN}_3 + \text{CO}_2$  chemical laser has been modeled and an experimental investigation conducted to determine the existence of laser action. The analytical model has been used to predict the expected population inversion and laser gain for a range of pressures and various additives. The experimental investigation conducted for comparison with the model did not result in laser action. The increase in pressure for the mixtures investigated indicates the occurrence of an explosion. The lack of detection of laser action has been attributed to difficulties with alignment of the optical system and to signal noise associated with the flash circuit.





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# TABLE OF SYMBOLS

$A_{ij}$	Einstein Coefficient
$B$	Rotational constant
$C$	Speed of light
$C_v$	Specific heat at constant volume
$E_{\text{thermal}}$	Excess energy released by a reaction
$h$	Planks constant
$H$	Photon energy
$J$	Rotational level
$K$	Boltzman's constant
$M$	Molecular weight
$N_{\text{CO}_2}$	Total number density (per unit volume) of $\text{CO}_2$
$N_{\text{II}}$	Number density (per unit volume) of $\text{CO}_2$ in Mode II
$N_{\text{I}}$	Number density (per unit volume) of $\text{CO}_2$ in Mode I
$R_i$	Reaction rate
$T$	Translational temperature
$X_i$	Volume concentration of chemical species
$\lambda_{ii}$	Radiative wave length (10.6 microns for $\text{CO}_2$ )
$\mu$	Reduced mass





## ACKNOWLEDGEMENTS

The author wishes to express his gratitude to Dr. D. J. Collins for his consultation and guidance. I very much appreciate his patience and advice throughout the period of this investigation.

I wish to extend a special note of thanks to Norman E. Leckenby for his technical assistance.



## I. INTRODUCTION

The first laser action was observed by Maiman in 1960. Many different laser systems have since been investigated. One of the most promising systems of efficient laser energy is the chemical laser. Since the energy is stored within the laser medium itself, the chemical laser is of technological interest for its simplicity and compactness. The ability of such a laser to provide insight into the distribution of chemical energy in the products of a reaction make it an attractive tool for understanding complex reactions.

The most favorable reactions for the production of laser action are those which are highly exothermic and involve the formation of products in high energy states. Such reactions are most commonly of the branched-chain type. The excited products may be electronically or vibrationally excited. However, they must be in a state sufficiently differing from equilibrium so as to be capable of producing a population inversion either within the products or by energy transfer to an additive.

The latter method has been extensively investigated using carbon dioxide as an additive; and is the process of interest in the Hydrogen Azide-Carbon Dioxide ( $\text{HN}_3 + \text{CO}_2$ ) laser. The explosive decomposition of  $\text{HN}_3$  produces vibrationally excited nitrogen which subsequently, through near resonant energy transfer, produces a population inversion within the vibrational levels of  $\text{CO}_2$ . The laser action then occurs through stimulated emissions from the asymmetric vibration level ( $\nu_3$  level) of  $\text{CO}_2$ .



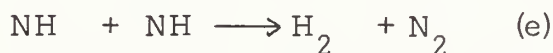
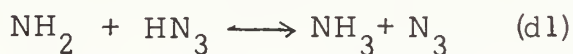
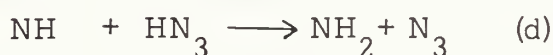
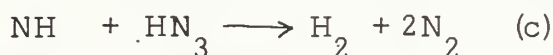
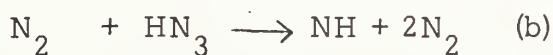
In the following sections a detailed description of the reaction mechanisms involved in the  $\text{HN}_3 + \text{CO}_2$  laser will be presented. The explosive decomposition of  $\text{HN}_3$  and the resulting laser gain have been analytically modeled to gain an insight into the potential of the laser. In addition, an experimental investigation has been conducted in order to determine the existence of laser action and applicability of the model.



## II. THEORY OF HYDROGEN AZIDE EXPLOSION

Hydrogen Azide ( $\text{HN}_3$ ) is an unstable endothermic gas at room temperature. It is known to explode violently even in the absence of oxygen, above certain limits of temperature and pressure. At low pressures, less than 40 mm Hg, it is a relatively stable compound. However, the stoichiometric process by which  $\text{HN}_3$  reacts at these pressures is not constant (Ref. 1). This has hampered the investigation and understanding of the mechanisms by which the reaction proceeds.

The generally adopted reaction mechanism of  $\text{HN}_3$  is (Refs. 1 - 7):



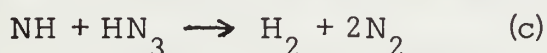
Domination of reaction (c) results in a violent explosion while reaction (d) leads to a slowing and eventual quenching of the reaction. The rates at which the two mechanisms proceed are a function of the pressure of  $\text{HN}_3$ , the method of initiation, and the type and quantity of any diluent (Ref. 7).





Initiation of  $\text{HN}_3$  by spark discharge and flash photolysis lead to a domination of reaction (c) while slow thermal decomposition follows reaction (d). However, spark discharge and flash photolysis initiation may still result in the quenching of the explosion by reaction (d) if the dilution of  $\text{HN}_3$  is sufficiently high.

Several investigators have suggested reaction (c) be divided into reactions:



The presence of  $\text{H}_2\text{N}_2$  has not been experimentally observed and reaction c' is 5 Kcal mole<sup>-1</sup> less exothermic than reaction (c). In addition,

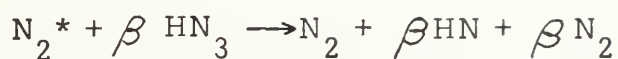
$\text{H}_2\text{N}_2$  is a relatively stable compound. Therefore it is assumed that if the reaction of NH with  $\text{HN}_3$  proceeds via a highly excited  $\text{H}_2\text{N}_2$  particle, it would decompose preferentially into  $\text{H}_2 + \text{N}_2$ .

Reaction (b) as a propagation step has not been observed experimentally, however, it has been suggested as the probable mechanism (Refs. 2,3). The vibrational excitation of nitrogen is consistent with the observed lasing action obtained from the reaction of  $\text{HN}_3$  when diluted with  $\text{CO}_2$  (Refs. 11,12). It is energetically feasible since there is sufficient excess energy from flash photolysis and reaction (c) to produce vibrationally excited  $\text{N}_2$  capable of reacting with  $\text{HN}_3$  (Ref. 2).

V. G. Voronkov et. al. (Ref. 8) has suggested a totally different reaction mechanism in which the propagation and branching reactions



are interchanged:



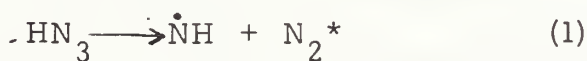
$\text{N}_2^*$  is vibrationally excited and capable of decomposing  $\beta \text{HN}_3$  molecules. These reactions are plausible; however, A. S. Rozenberg and V. G. Voronkov (Refs. 9, 10) in later publications have followed the generally accepted reaction mechanism. Therefore the possibility of the interchange of these reactions has not been considered.



### III. ANALYSIS OF HN<sub>3</sub> EXPLOSION

If the concentration limits and method of initiation are restricted, an analysis of the explosive decomposition of HN<sub>3</sub> is possible. Since an explosion is necessary for lasing to occur and the method of initiation has been chosen as flash photolysis, prediction of the products of the explosion will allow the laser to be modeled.

Provided the dilution of HN<sub>3</sub> is not sufficient to inhibit an explosion, reaction (d) may be neglected since the products of the reaction have not been experimentally observed (Refs. 1, 4). The equations necessary to describe the explosion become:



$$\frac{dT}{dt} = f(\text{time}, \Delta E) \quad (6)$$

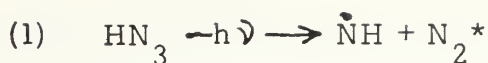
\* N<sub>2</sub> in its ninth vibrational level or higher

' N<sub>2</sub> in less than its ninth vibrational level

• NH in its a'<sup>1</sup>Δ electronic state

These reactions are divided into sections according to their number so the assumptions and calculations necessary to the model may be stated in detail.





Photochemical decomposition of  $\text{HN}_3$  was first investigated by Beckman and Dickerson who showed the quantum yield to be  $3.0 \pm 0.5$  and independent of pressure between 2 and 130 mm. of mercury. Flash photolysis of  $\text{HN}_3$  has been studied by Cornell, Berry, and Lwowski (Ref. 13) and Thrush (Ref. 4). They detected the presence of the NH radical and identified it in its ground electronic state. Okabe's (Ref. 3) and Welge's (Refs. 14, 15) recent investigations of vacuum-uv photolysis have shown the primary photochemical process in the dissociation of  $\text{HN}_3$  to result in  $\text{N}_2$  and NH in their  $\text{X}' \sum_g^+$  and ( $\text{a}'\Delta$  or  $\text{X}^3 \sum^-$ ) states respectively. Okabe also reported that Stuhl (Ref. 16) detected these as the primary states resulting from flash photolysis. Konar et. al. (Ref. 17) has suggested  $\text{N}_2$  to be in a vibrationally excited ground electronic state since selection rules preclude both  $\text{N}_2$  and NH from being electronically excited.

It is assumed that NH is formed in its  $\text{a}'\Delta$  state, having a total energy of 61 Kcal. mole<sup>-1</sup>. For an average quantum wave length of 2125°A the total energy available for dissociation is 154 Kcal. mole<sup>-1</sup>, thus leaving an average of 93 Kcal. mole<sup>-1</sup> to be shared between the vibrational states of NH and  $\text{N}_2$ . The principle of equal parittion of energy indicates that nitrogen should be in its ninth vibrational level, thus having an excess energy of 60 Kcal. mole<sup>-1</sup>, more than sufficient for decomposition of  $\text{HN}_3$ . The remaining 13 Kcal. are assumed to be absorbed as translational energy.





The rate constant for the photolysis of  $\text{HN}_3$  may be calculated if the absorption coefficient, quantum yield and energy of the flash is known. The rate of decomposition of  $\text{HN}_3$  depends on the photon flux from the flashlamp, its absorption coefficient and the quantum yield and is given by (Ref. 18):

$$R_{\text{HN}_3} = \overline{\text{KHV}} [\text{HN}_3] = \phi (1 - e^{-\alpha \ell}) Q$$

where  $\phi$  is photon flux,  $Q$  the quantum yield,  $\alpha$  the absorption coefficient,  $\ell$  the optical thickness of the absorber and  $\overline{\text{KHV}}$  the average rate constant.

The average photon flux may be calculated from:

$$\phi = \frac{E_o \xi \Delta \nu_{\text{HN}_3} G}{\Delta t h \nu_{\text{HN}_3} \Delta \nu_{\text{fl}}}$$

where:  $E_o$  is the energy stored in the capacitor bank

$\xi$  the efficiency of the flashlamp

$\Delta t$  pulse duration

$\Delta \nu_{\text{fl}}$  flash spectral range

$\Delta \nu_{\text{HN}_3}$  absorption band of  $\text{HN}_3$

$\nu_{\text{HN}_3}$  center frequency of  $\text{HN}_3$  absorption band

$h$  Planks constant

$G$  geometrical relation between the laser tube and flashlamp

For a discharge energy of 1000j the ILC 7L24 lamp has an efficiency of 85% over the range  $\Delta \nu_{\text{fl}} = 2000^\circ\text{A}$  to 4 microns. The absorption coefficient of  $\text{HN}_3$  is 25 at one atmosphere and a center band frequency



of  $\lambda_{\text{HN}_3} = 2125^\circ\text{A}$ . The absorption band ( $\Delta\lambda_{\text{HN}_3}$ ) of  $\text{HN}_3$  is between  $2000^\circ\text{A}$  and  $2250^\circ\text{A}$ . The quantum yield is 2.0 (Ref. 5). The geometrical relation between the flashlamp and laser tube is based on the product of the angle which the laser tube subtends on the flashlamp and the reflector coupling of the cavity mirrors. The angle subtended by the laser tube utilized in this investigation was 0.2 of the total flash angle and the reflector coupling factor was assumed to be 2.5 (Ref. 19). These values yield a photon flux of:  $\phi = 5.4 \times 10^{23}$  photons/sec.

The average rate constant for the decomposition of  $\text{HN}_3$  may be calculated from the rate equation:

$$\overline{\text{KHV}} = \phi (1 - e^{-\alpha l}) Q/[\text{HN}_3]$$

$\alpha$  is independent of pressure, and the average concentration of  $\text{HN}_3$  in the laser tube has been taken as  $10^{18}$  particles/cc. Substitution of the above quantities into the equation yield an average rate constant of  $3.23 \times 10^2 \text{ sec}^{-1}$ .

From the experimental flash profile the rate of decomposition of  $\text{HN}_3$  as a function of time may be determined. This profile is shown in Figure 15 and may best be described by a cubic equation:

$$\text{KHV} = at^3 + bt^2 + ct + D$$

From the average rate constant and the experimental profile the boundary conditions on the above equation become:



$$t = 0 \quad KHV = 0$$

$$t = 100 \text{ usec.}, \quad KHV = 0$$

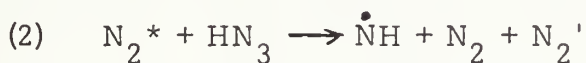
$$t = 37.5 \text{ usec.}, \quad \frac{dKHV}{dt} = 0$$

$$\frac{1}{t} \int_{t=0}^{t=100} KHV dt = \overline{KHV}$$

The above boundary conditions yield a rate constant of

$$KHV = 2.89 \times 10^{15} t^3 - 6.4 \times 10^{11} t^2 + 3.42 \times 10^7 t \text{ where } t \text{ is in seconds.}$$

This rate constant results in total decomposition of  $\text{HN}_3$  at a pressure of 6 torr. When 25 torr of  $\text{HN}_3$  that is sufficiently diluted to prevent an explosion, only 9.5% of the  $\text{HN}_3$  is decomposed.



The reaction of  $\text{N}_2^*$  and  $\text{HN}_3$  as the propagation equation for the branched-chain explosion explains the observed dependence on various diluents and hydrocarbon scavengers (Ref. 2). Inorganic diluents do not significantly reduce the rate of formation of products for volume ratios of diluent to  $\text{HN}_3$  less than 10. For ratios greater than 10 they slowly decrease the rate of production of products to a maximum of 30% at dilutions of 100 and greater. Hydrocarbon scavengers however have a marked effect and reduce the rate by 70% for dilution ratios less than 10 (Ref. 2). This suggests that inorganic diluents do not react with the excited  $\text{NH}$  as do the hydrocarbons. Instead they merely increase the rate of relaxation of the vibrationally excited  $\text{N}_2$ . Since the vibrational



levels of  $N_2$  below the ninth are not sufficiently excited to react with  $HN_3$ , this increase in relaxation rate is reflected in the slowing of reaction (2).

Nitrogen particles in vibrational levels above the ninth have been assumed to be in the ninth level. The number of particles in these levels are negligible at room temperature. At higher temperatures the rate of relaxation to a Boltzman distribution in the lower levels is a minimum of ten times faster than the excitation to levels above the ninth.

The rate constant for the reaction of  $HN_3$  with excited nitrogen has been given by Okabe (Ref. 3) as approximately  $10^{11} \text{ cm}^3 \text{ moles}^{-1} \text{ sec}^{-1}$  at  $300^\circ\text{K}$ . In order to obtain the temperature dependence of reaction (2), the activation energy of the reaction has been calculated and the rate is assumed to obey an Arrhenius equation ( $K = Ae^{-E_a/RT}$ ). The constant A may then be determined from the known value of the rate constant at  $300\text{K}$ .

The activation energy has been calculated from Simple Collision Theory (Ref. 20). The relative Kinetic energy along the line of centers of the two approaching molecules is given by:

$$E_r = \frac{1}{2\mu} \left[ M_a^2 v_a^2 + M_b^2 v_b^2 \right]$$

where:  $M_i$  is the mass of reactant i

$V_i$  is the mean molecular velocity of i

$\mu$  is the reduced mass





The activation energy is related to the  $E_r$  in Simple Collision Theory by:

$$E_a = E_r + \frac{RT}{2}$$

where:  $T$  = temperature in  $^{\circ}\text{K}$

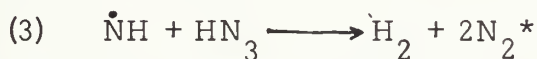
$R$  = universal gas constant

The mass of  $\text{N}_2$  is 28.01 and  $\text{HN}_3$  is 43.0. At a temperature of  $300^{\circ}\text{K}$  the above equations yield an activation energy of 6.42 Kcal/mole. The constant  $A$  can then be obtained from the Arrhenius equation at a temperature of  $300^{\circ}\text{K}$ :

$$A = K e^{E_a/RT} = 7.64 \times 10^{-9} \text{ cm}^3 \text{ part}^{-1} \text{ sec}^{-1}$$

and the rate constant can then be expressed as a function of temperature:

$$K_2 = 7.65 \times 10^{-9} e^{-6400/RT} \text{ cm}^3 \text{ part}^{-1} \text{ sec}^{-1}$$

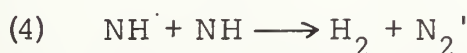


The interaction of  $\dot{\text{N}}\text{H}$  with  $\text{HN}_3$  is highly exothermic and involves the formation of several bonds which is indicative of a branched-chain reaction, and the creation of vibrationally excited particles (Ref. 21). Since the energy released in such a reaction is concentrated along the bonds of the products, and with the previous assumption of the principle of equal partition of energy, it is assumed that all the nitrogen formed is in the ninth vibrational level. Hydrogen's vibrational levels are much more widely spaced than those of  $\text{N}_2$  and it has no low-lying electronic state which could be excited. The participation of hydrogen as a reactant has not been experimentally observed and therefore it is assumed that if hydrogen is formed in an excited state its energy is quickly dissipated into translational energy.



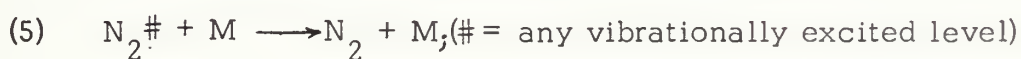
The rate constant for the reaction of  $\text{HN}_3$  with various  $\text{NH}$  radicals has been determined by Okabe (Ref.3). Assuming all  $\text{NH}$  formed to be in the  $a'\Delta$  state the rate of reaction (3) is  $5.5 \times 10^{11} \text{ cm}^3 \text{ moles}^{-1} \text{ sec}^{-1}$  at  $300^\circ\text{K}$ . The temperature dependence of the rate constant for reaction (3) has been determined by the same method as that of reaction (2) and has the value of:

$$K_3 = 8.7 \times 10^{-7} e^{\frac{-8210}{RT}} \frac{\text{cc}}{\text{part. sec.}}$$



Reaction (4) is relatively slow and may be neglected in the prediction of the explosion characteristic of  $\text{HN}_3$  (Ref. 10). It does, however, serve to explain the long lasing time observed from an explosion of  $\text{HN}_3$  and  $\text{CO}_2$ ; therefore it is included in the model. The rate constant has been obtained from Reference 33 and is:

$$K_4 = 3.6 \times 10^{-12} T^{0.55} e^{\frac{-1900}{RT}} \frac{\text{cc}}{\text{part. sec.}}$$



In order to predict the effect of inorganic diluents on the explosion, the collisional deactivation of  $\text{N}_2^\#$  must be included. Reaction (5) is not kinetically correct but merely representative of the process. The actual process may be divided in two parts: collisional relaxation of pure nitrogen and the effects of additives.

The derivation of the multi-quantum level population equation is shown in detail in Reference 22 and will not be repeated here. The only assumption involved in the derivation is that transitions are only



allowed between adjacent quantum levels. The validity of this assumption is supported by the agreement obtained with experimental results (Ref. 22). The general equation for the vibrational relaxation of pure nitrogen is given by:

$$\frac{dN_m}{dt} = -K_{m,m+1}N_m - K_{m,m-1}N_m + K_{m+1,m}N_{m+1} + K_{m-1,m}N_{m-1}$$

where  $K_{ij}$  is the transition rate for  $N_2$  to or from the  $m^{\text{th}}$  vibrational level.

The transition rates for pure nitrogen have been obtained from Reference 24 (translational-vibrational) and Reference 28 (vibrational-vibrational) and are:

$$\begin{aligned} \text{T-V transitions} &= 7.34 \times 10^{21} T^{-1} e^{(-290.4 T^{-1/3} - 12.5)} \quad T = 1950 \\ &= 7.34 \times 10^{21} T^{-1} e^{(-56.7 T^{-1/3} - 31.2)} \quad T = 1950 \\ \text{V-V transitions} &= 9.65 \times 10^3 T^{1/2} \end{aligned}$$

where:  $T$  is in degrees Kelvin and the rates in  $\text{sec}^{-1}$ .

The increase in vibrational relaxation of  $N_2$  by diluents depends primarily on how well matched the vibrational levels of the diluents are to those of nitrogen. The process of vibrational energy transfer for molecules having exactly matched levels is extremely efficient, occurring approximately every 400 collisions, while the probability of energy transfer for levels differing greater than  $200 \text{ cm}^{-1}$  may be assumed negligible for most reactions (Ref. 22).



The  $\nu_3$  level of carbon dioxide ( $\text{CO}_2$ ) and the  $\nu_1$  level of nitrogen differ by only  $18 \text{ cm}^{-1}$  and therefore an extremely efficient near-resonant energy transfer occurs between these levels. The effect on the explosion by  $\text{CO}_2$  and additional diluents of interest to the  $\text{HN}_3$  laser are shown in Figure 1.

#### (6) TEMPERATURE AS A FUNCTION OF TIME

The final quantity necessary for prediction of the products of the explosive decomposition of  $\text{HN}_3$  is the variation of the translational temperature with time. In a constant volume system this increase in temperature is due primarily to the energy evolved from the reaction into the translational and rotational motion. Since the relaxation of the rotational levels of a molecule are characteristically on the order of nano-seconds, the energy liberated into rotational energy may be considered as a direct increase in the translational temperature (Refs. 23, 24).

The equation for the raise in translational temperature as a function of time may then be expressed as:

$$\frac{dT}{dt} = \frac{\sum E_{\text{thermal}}^R}{\sum C_v [X_i]}$$

The above reactions have been programmed and numerically integrated on the IBM 360 computer. The resultant temperature from the explosion has been compared with the experimental results of A. S. Rosenberg and V. C. Voronkov (Ref. 9) in Figure 1. Exact agreement is not to be expected since the experimental data were obtained from explosions resulting from initiation by a minimum electrical discharge.





#### IV. ANALYSIS OF THE $\text{HN}_3 + \text{CO}_2$ LASER

The extension of the  $\text{HN}_3$  explosion model to allow calculation of laser gain may be accomplished relatively easily. The primary equations (effects of diluents on  $\text{N}_2$ ) for the prediction of gain are contained in the explosion model. It is only necessary to consider in greater detail the vibrational relaxation of  $\text{CO}_2$  and its energy transfer with the vibrationally excited nitrogen evolved from the explosion.

This vibrational energy transfer process may be described by dividing the vibrationally excited levels of  $\text{CO}_2$  into three modes (Ref. 25). As shown in Figure 2, mode 0 contains only  $\text{CO}_2$  molecules in their ground vibrational level, mode I those in the symmetric and bending levels, and mode II being those in the asymmetric stretching level.

The energy of the asymmetric stretching level (mode II) of  $\text{CO}_2$ , as previously noted, is near resonant with the  $v_1$  level of  $\text{N}_2$ , therefore resulting in a quantum energy transfer approximately every 465 collisions (Ref. 25). In addition,  $\text{N}_2$  in its ground electronic state has a zero permanent dipole moment and cannot decay to its ground vibrational level through electric-dipole radiation. Its first vibrational level is metastable, thus being ideal for the selective excitation of the asymmetric stretching level of  $\text{CO}_2$ .

The  $V_3$  level of  $\text{CO}_2$  is also metastable, having (at 420°K and a total pressure of 15 torr) a radiative lifetime on the order to four seconds



and a collisional de-excitation rate of  $4 \times 10^{-2}$  seconds (Ref. 25). The levels of mode I at the same conditions have an overall relaxation time of approximately 20  $\mu$ -seconds, being limited primarily by the (01'0) level (the lowest vibrational level of  $\text{CO}_2$ ) which required 18  $\mu$ -seconds for deactivation. This large difference in relaxation times allows the inversion mechanism by which lasing action may be obtained.

The mechanism of stimulated emission (lasing action) in the  $\text{CO}_2$  molecule is characterized by transitions between two vibrational levels. The upper level in  $\text{CO}_2$  is the asymmetric stretching level (001) while the lower level is the symmetric level (100). The symmetry of carbon dioxide allows only odd rotational levels in the upper vibrational level and only even in the lower level (Ref. 26). Laser transitions occur between particular rotational levels within the vibrational levels, and correspond to a rotational quantum change of  $J=\pm 1$ . Changes of  $J=+1$  are P-branch transitions and result in a higher gain than those of  $J=-1$  which are R-branch transitions. Since lasing action occurs first from the rotational level of the highest gain which is subsequently fed by other levels to maintain a Boltzman distribution (requiring less than  $10^{-7}$  sec.), R-branch transitions do not occur (Ref. 27). This results in a laser emission at a wavelength of 10.6 microns.

In order to calculate the energy output from the  $\text{HN}_3 + \text{CO}_2$  laser, the number of molecules in each vibrational level of  $\text{CO}_2$  must be known as a function of time. However, since the vibrational levels of  $\text{CO}_2$  greater than (00°1) have an extremely fast relaxation time (200 n-sec at



420°K and 15 torr) and the relaxation of the lower level (100) is limited by the depopulation of the (010) level to the ground state, the population inversion and gain may be calculated within 5% from the knowledge of the total number of molecules within modes I and II (Ref. 25). Considering the assumptions made in prediction of the products of the explosion this is sufficient accuracy. The equations for the population inversion and gain are:

$$PV = (N_{\text{mode II}} - N_{\text{mode I}}) / N_{\text{CO}_2}$$

$$G_o = \frac{h}{8\pi K} \sqrt{\frac{MC^2}{2\pi K}} \frac{\lambda_{21}^3}{T^{3/2}} A_{21} (2J+1) B (N_{\text{II}} - N_{\text{I}}) e^{-(BJ(J+1)) \frac{hc}{KT}}$$

where: PV = population inversion

$$G_o = \text{gain}$$

Other symbols have their usual quantum mechanical meaning and are listed in the TABLE OF SYMBOLS.

The reactions and rate constants which must be added to the explosion model to determine the above quantities are given in Appendix A. The kinetic rate equations have been numerically integrated using Fortran IV language on the USNPGS IBM 360 computer. A parameter variation based on the above assumptions has been carried out and the results plotted in Figures 3 and 4. These will be discussed in the Results section.



## V. HN<sub>3</sub> + CO<sub>2</sub> LASER PROGRAM

Equations 1-6 (Appendix A) result in a set of first order linear differential equations. These equations may be integrated to determine the products as a function of time if the rate constants and initial concentrations of the reactants are specified. This integration has been carried out numerically on the USNPGS IBM 360 computer.

The program and a sample output is shown in Appendix B. The relation between computer and usual notation is contained on comment cards within the program. A region of 100K and an average computer time of five minutes is required to predict laser gain.

The USNPGS RKLDEQ library subroutine, employing a Runge-Kutta-Gill predictor-corrector method, has been used to numerically integrate the rate equations. In addition, a variable step size based on temperature has been provided to reduce computer time. Integration is accomplished on a particle per cubic centimeter basis and double precision accuracy (16 significant digits) has been employed to minimize mathematical error.

Data output is controlled by numerically recording every tenth step while laser gain and population inversion are graphically displayed every step once the gain becomes greater than  $10^{-5}$ . The subroutine OSPLOT has been used for plotting gain and population inversion. It





allows an unlimited number of points to be plotted and requires only 0.2 seconds of computer time to plot an average of 200 points.

The sample program in Appendix B is capable of calculating laser gain, population inversion, and vibrational temperature for the  $\text{HN}_3 + \text{CO}_2$  laser with additional diluents of helium, nitrogen or hydrogen. Lasing action and cavity losses have not been considered in the model. If investigation of other inorganic diluents is desired, it may be accomplished by setting He (Helium) in the program equal to the diluents concentration and changing the rate constants specified in the program, to those of the diluent of interest.

The results obtained (Appendix B) allow determination of affects of pressure and diluent variation on the laser gain and population inversion. The assumptions necessary to model the explosion are the limiting factors to the accuracy of the results. Experimental determination of the rate constants for reactions 2 and 3 would resolve this limitation. Experimental observation of laser action would also aid in determination of the quantitative accuracy of the model.



## VI. EXPERIMENTAL TECHNIQUES

A chemical laser requires the integration of several very different systems. These apparatus may be divided into five categories:

(a) general description; (b) flash equipment; (c) chemical and vacuum systems; (d) laser cavity; (e) recording equipment. This allows a more detailed description of each system and its function in a chemical laser.

### A. GENERAL DESCRIPTION

A general block diagram of the laser components is shown in Figure 5. The flashlamp, laser cavity and toxic gas systems are located in a fume hood due to the toxic and explosive nature of the chemicals involved in the generation of  $\text{HN}_3$ . The fume hood is exhausted to the atmosphere by a fan and has been fitted with a plexiglass covered extension for greater ease in weighing chemicals.

To the left of the fume hood is the main control panel and the remainder of the gas system containing non-toxic, non-reactive gases. All systems can be operated from the main panel with the exception of charging the circuit capacitor bank. In addition, all recording equipment is located in this area for greater safety. On the right is the trigger circuit, electrical control box, capacitor bank, and the charging circuit for the flash system.

Considering the high voltages involved in the flash equipment and the explosive nature of the chemicals, the two systems have been



separated wherever possible. During all experiments the operator is located in area to the left of the fume hood to minimize contact with the high voltage systems. The extension to the fume hood is fitted with rubber seals and in combination with the exhaust fan provides a sub-atmospheric pressure in the interior insuring an air flow away from the operator. The safety features of each system will be covered in the detailed description of the categories below.

## B. FLASH EQUIPMENT

The flash system contains three electrically separated circuits: the discharge circuit, triggering circuit, and charging circuit. The three components are integrated through the electrical control box (Fig. 6) located to the right of the fume hood. The entire flash system can be monitored and fired through the control box. However, an additional firing switch has been installed on the main control panel for greater safety.

The discharge circuit (Fig. 7) is a simple series circuit containing the flashlamp, capacitor bank and inductance coil. These may be varied in accordance with Reference 30 to obtain the desired pulse duration and energy output. The flashlamp parameters specified by the manufacturer determine the bounds within which the system may be operated. The flashlamp is a xenon filled, ILC model 7L24 (60 cm. by 7 mm.), lamp with nickel plated copper electrodes. A lamp with either a natural or synthetic quartz envelope may be used in the circuit as designed.



The former emits light of 2000°A and greater while the latter's emission band starts at 1600°A. The synthetic quartz lamp is particularly useful for decomposition of  $\text{HN}_3$  which has an absorption band that rises sharply below 2000°A. However, in order to obtain the full effectiveness from the lamp the laser tube must also be made of synthetic quartz. The 7L24 lamp with either envelope has an impedance factor of 116 and requires a minimum trigger voltage of 25KV for 2.4 micro-seconds.

The other two components of the system are the capacitor bank, consisting of four  $7\ \mu\text{f.}$  and two  $1.5\ \mu\text{f.}$  high voltage (25KV capability) capacitors in parallel, and a  $30.0\ \mu\text{h}$  inductance coil made of 3/8-inch copper tubing consisting of 25 windings 15 cm. in diameter. The components have been silver soldered in series using  $3 \times 1/4$ -inch copper bars and 3/8-inch copper tubing. The measured ohmic resistance of the circuit is 0.0013 ohms and can be neglected in the calculation of the operating parameters.

The flash circuit has been designed for a damping factor of 0.8 and a pulse duration of  $100\ \mu\text{-sec.}$  with an energy output of 2000 joules. The lamp may be operated under manufacturer's warranty, with a damping factor of 1.1 to 0.7. This allows a variation of energy output with a minimum increase or decrease in pulse duration. The energy output variation with capacitor bank voltage has been calculated from Reference 30 for the allowable damping factor range. Figure 8 shows the energy output in joules for a given capacitor bank voltage.





The triggering circuit creates an ionized spark streamer between the two electrodes which allows the main discharge to occur. It is external to the flashlamp (Fig. 9) and consists of a Dressen-Branes 300 volt, 70  $\mu$ a DC power supply, an 8  $\mu$ f. oil filled capacitor, SCR, and a ILC model T105 trigger transformer with a step-up ratio of 60:1. The circuit is controlled by a relay that is energized by pressing the firing switch. A detailed circuit diagram is shown in Figure 9.

The charging circuit consists of a NJE (New Jersey Electronics) Model HA-51 variable high voltage power supply (0-30kv, 0-10 $\mu$ a) which is connected through a high voltage vacuum switch to the capacitor bank in series with a 3m $\Omega$  resistor (Fig. 10). When the charge/dump switch is placed in the charge position, the capacitor bank voltage is monitored on a 20  $\mu$ a API (Assemble Products, Inc.) meter relay on the electrical control box. The meter is calibrated as a voltmeter and interrupts the charging, by isolating the charging circuit and placing the system in the ready-fire position, when the set voltage is reached. A warning flasher is mounted on the control box and is activated at any time the charge/dump switch is placed in the charge position.

Safety is of prime importance to the flash system. With the exception of the flashlamp, the entire system has been placed on the side of the laboratory away from the operator's position during experiments. The flasher on the electrical control box is automatically activated when charging is initiated. The relay meter which separates the charging system when the desired voltage is reached must be



electrically unslaved after firing before the system may be recharged. Plywood covers have been placed over the capacitor bank, inductance coil and high-voltage switches to minimize the danger of operator contact or possible arcing. As constructed, the system is easily operable while providing maximum operator safety.

### C. CHEMICAL AND VACUUM SYSTEMS

The chemical and vacuum systems have been integrated through a manifold mounted directly above the laser cavity in the fume hood (Fig. 11). All components of the toxic gas generator are contained under the fume hood while the inert gases and vacuum pump are external to the fume hood and connected to the manifold by 1/8-inch stainless steel tubing. The manifold consists of stainless steel valves that are operated by solenoids from the main control panel. This allows a fast and easy way to isolate any part of the system.

The toxic/explosive gas generator has been designed primarily for use in the generation of Hydrozoic Acid ( $\text{HN}_3$ ). However, it is capable of being used to generate other chemicals in a gaseous state. The description here will be concerned with the generation of  $\text{HN}_3$  since its design was for this purpose.

The gas generator is a 500 ml. pyrex flask (Fig. 12) fitted with a pyrex berrette graduated in cubic millimeters. A relief valve has been provided which opens to exhaust at atmospheric pressure to prevent possible damage from over pressure during generation of  $\text{HN}_3$ . The



system is connected to the manifold through a 1/4-inch pyrex U-tube by a combination of two ball joints and a flexible connection (bellows). The U-tube provides a convenient way of drying the  $\text{HN}_3$  with phosphorus pentoxide before it is introduced into the laser tube.

The generation of  $\text{HN}_3$  is accomplished by the following reaction (Ref. 31):



Sodium Azide ( $\text{NaN}_3$ : powdered solid) and phosphoric acid ( $\text{H}_3\text{PO}_4$ : 85% syrupy solution in water) are mixed according to their gram atomic weights to provide the desired amount or pressure of  $\text{HN}_3$  for the volume of the generation system. Table I shows the weights necessary to generate  $\text{HN}_3$  to pressures of 50mm, based on a one-liter system. If the present one-liter system is changed, the quantities of  $\text{NaN}_3$  and  $\text{H}_3\text{PO}_4$  necessary for generating the desired pressure of  $\text{HN}_3$  may be obtained by multiplying the data in Table I by the volume of the system. To generate a larger quantity of  $\text{HN}_3$  at the same pressure, the laser tube and pressure gauge may be left open during generation. This increases the volume from one to six and one-half liters.

Sodium azide is weighed and placed in the generation flask through the relief valve assembly and then mixed with Dow Corning 704 diffusion pump fluid (silicone based) DCC (Dow Corning Corp.) by means of a teflon coated magnetic stirrer in the bottom of the flask. The quantity of  $\text{H}_3\text{PO}_4$  used in the generation of  $\text{HN}_3$  is chosen slightly higher than stoichiometric to insure all  $\text{NaN}_3$  (explosive and toxic)



is consumed. After the system has been evacuated the  $\text{H}_3\text{PO}_4$  is introduced into the generation flask by a mechanically operated stopcock. The stopcock is controlled from a switch on the main control panel and rotates from fully open to fully closed in 15 seconds.

A plexiglass covered extension to the fume hood has been constructed to allow greater safety in the weighing and handling of the chemicals (Fig. 5). The extension has been sealed by the use of rubber stripping along the edges. A 14- by 12-inch door on one side allows the operator, wearing a face shield, easy access to all parts of the system while handling the chemicals. The exhaust fan provides an air-flow away from the operator, which is exhausted to the atmosphere, to prevent inhalation of toxic  $\text{HN}_3$  fumes.

The inert gas system is external to the fume hood and is connected to the manifold by 1/8-inch stainless steel tubing. The gases used in the laser were manufactured by ARC (Air Reduction Co., Inc.) and are supplied in one-liter pyrex flasks at a pressure of 755 mm of mercury. Their guaranteed purity is:

Carbon Dioxide	$\text{CO}_2$	:99.995%
Nitrogen	$\text{N}_2$	:99.999%
Helium	He	:99.9995%

Each gas is introduced into the laser tube by a separate solenoid switch. The quantity and rate of induction is controlled by needle valves located immediately behind the inlets. The pressure in the laser tube is monitored by a stainless steel bourdon tube gauge with a range from 0 to 800 mm of mercury and a precision of 0.1% full scale.





Prior to introducing the laser gas mixture the system is evacuated by a mechanical vacuum pump capable of producing a vacuum of  $10^{-3}$  torr. The system is flushed several times during evacuation with an inert gas ( $N_2$ ) to insure a minimum of impurities in the laser tube. Once evacuation is complete the desired mixture of  $HN_3$  and additional gases are introduced into the laser tube.

#### D. LASER AND OPTICAL CAVITY

The laser components are mounted on a one-meter standard optical bench (Figs. 13, 14). The laser tube is connected to the manifold, via a ball and socket joint, by 1/4-inch glass tubing which is sealed to a stainless steel bellows.

The laser tube is made of fused quartz and is 60 cm. long with an inner diameter of 30 mm. The ends of the tube have been cut and ground at a Brewster angle of  $56^\circ 40'$  (for sodium chloride) to minimize reflections. Sodium chloride windows were attached to the ends of the quartz tube by chemically inert silicone based cement.

The optical cavity is formed by two gold-surfaced concaved mirrors one inch in diameter placed 78 cm. apart in gimbal mounts made by Oleo Optical Co. The mirrors have a radius of curvature of ten meters. A 2-mm. hole drilled in the center of one mirror provides an output for the recording equipment and allows easy access to the cavity for alignment.



The amount of energy removed by the 2-mm. hole may be calculated from Gaussian theory and is directly related to the laser beam spot size (Ref. 32). This becomes important when small gains are involved and will be discussed in the results section. For the laser cavity described above, Gaussian theory yields a spot size 6.0 mm. in diameter for a wavelength of 10.6 microns and energy removal of 37%. This applies to the lowest order mode. Higher order modes which exist in the comparatively large diameter laser tube extend further in the transverse direction, thus most of their energy is off the axis of the resonator.

Alignment of the laser cavity and recording equipment is comparatively critical and conditions for stability of the cavity are given below:

$$0 \leq g_1 g_2 \leq 1$$

$$L = R_1 R_2$$

Where

$$g_1 = 1 - \frac{L}{R_1}$$

$$g_2 = 1 - \frac{L}{R_2}$$

$L$  = length of the cavity

$R_1$  = radius of the mirror

The alignment is accomplished using a commercial He-Ne laser with a continuous output of one milliwatt. The He-Ne laser is placed in line with the laser cavity and its beam is passed through the 2 mm. hole in one of the cavities' mirrors. The mirrors are then adjusted until all



reflections within the cavity pass back through the hole and directly into the He-Ne laser. The limit to the precision of alignment ( $2 \times 10^{-4}$  radians) is the smallest adjustment which can be made with the gimbal's micrometers.

#### E. RECORDING EQUIPMENT

In order to effectively monitor the light output from the laser cavity two detectors were used. This allowed the flashlamp discharge to be recorded by one detector while the other was being used in conjunction with various filters to determine any resulting laser energy. The two detector signals were recorded on a dual beam oscilloscope during each experiment. The position of the two detectors in the experimental setup is shown in Figures 13 and 14.

A photo-diode detector was used to monitor the flashlamp discharge. It provided an effective method of monitoring the lamp pulse duration and relative magnitude for various capacitor bank voltages. In addition, it served as the triggering device for the oscilloscope, thus providing a reference for the second detector.

For detection of laser energy a gold-doped germanium detector was used in conjunction with several filters. The detector is cooled by liquid nitrogen and biased controlled to yield a signal of several millivolts. Its maximum response time is 50 nanoseconds over a range of 1.0 to 10.0 microns. Because of the detectors high sensitivity, a monochromator and several different filters were employed in order to eliminate extraneous light.



A Perkin-Elmer Grating monochromator (MG-12b) with a blaze angle of 12 microns was used to monitor a specific wavelength of light. It was calibrated with a He-Ne laser and cross-checked with a mercury light. When the doors of the monochromator are fully open (2 mm.), a wavelength band of 0.3 microns was provided to the detector, thus eliminating the requirement of filters to attenuate the light signal.

Two different filters were employed without the monochromator in an effort to determine lasing action that might have occurred in a range not allowed by the monochromator. First, an Irtran II filter which passes light between 2.0 and 12 microns was used. However, due to the amount of light emitted in this range by the flashlamp, the oscilloscope vertical scale deflection was limited to 50 millivolts per cm. This was an order of magnitude greater than the expected laser signal and limited determination of any output. A KBR filter passing light only above 10.2 microns was also employed. It allowed oscilloscope deflection as small as 5 millivolts per cm. but eliminated detection of the 9.4 micron band of  $\text{CO}_2$ .

A sample output of each recording setup is shown in Figures 15 and 16. The oscilloscope vertical response time is 0.06  $\mu$ -seconds and scale deflection settings are shown beside each trace. The minimum detectable response is considered to be five millivolts in all cases, due to radiation noise from the flash circuit discharge.





## VII. RESULTS

### A. THEORETICAL

The agreement of the computer model with the experimental adiabatic temperature (Fig. 1) obtained in Reference 9 showed maximum difference of 9%. This lends some support to the many assumptions necessary to model the explosion. Since the rate constants for reactions (b and c) had to be calculated from sparse experimental data, the determination of exact rate constant as a function of temperature would considerably strengthen the model.

From the large amount of data obtained from the computer model, three factors are of major interest to the experimental investigation of the laser. First is the magnitude of the laser gain for mixtures of  $\text{HN}_3 + \text{CO}_2$ . Second, the duration for which the gain is sufficiently high that it may be experimentally observed. And last, is the effect of the addition of He to the laser mixture. These factors have been graphically displayed in Figures 3 and 4.

Figure 3 shows laser gain as a function of the dilution ratio of  $\text{CO}_2$  to  $\text{HN}_3$ . The ratios for which gain is obtainable is broadened as the pressure of  $\text{HN}_3$  is reduced. This is indicative of a total pressure limitation on the laser. For 40 torr of  $\text{HN}_3$  and a total pressure of 150 torr the vibrational relaxation rate of  $\text{CO}_2$  becomes comparable to the reaction rates of the explosion which precludes laser gain. In addition, the maximum pulse duration occurs at dilution ratios less



than those of maximum gain. The pulse duration falls slowly on either side of the maximum. This becomes important in the experimental observation of laser action only at high pressures where the pulse duration approaches the response time of the experimental recording equipment.

The effects of the addition of He to the laser mixture are quite pronounced. A significant increase in gain as well as pulse duration results. Figure 4 shows increase in gain with dilution of He for 25 torr of  $\text{HN}_3$ . With 100 torrs He added to the mixture, the gain is more than doubled and the maximum pulse increases from 5 to 26  $\mu\text{sec}$ . Further increases in He results in a slight decrease in gain while the pulse duration remains nearly constant. However, dilutions of greater than 4 to 1 for He is approaching the lower limit of the model where the reactions neglected become important.

From the results of the computer model, it would appear that laser action could be obtained even in the crudest of experimental setups. However, two things have not been considered in modeling the  $\text{HN}_3 + \text{CO}_2$  laser. The actual particle depletion that results from laser radiation and the possibility of a reaction involving  $\dot{\text{N}}\text{H}$  and  $\text{CO}_2$ . The addition of the former requires a significant increase in the number of assumptions necessary for modeling the laser and could well degrade the accuracy of the results. The latter would only be speculation since very little is known about the reaction of  $\dot{\text{N}}\text{H}$  with any molecule. The limitations and accuracy of the model are contingent on experimental observation of laser action.



## B. EXPERIMENTAL

An experimental investigation of the  $\text{HN}_3 + \text{CO}_2$  laser was conducted for pressures of  $\text{HN}_3$  from 6 to 35 torr. In addition to pure  $\text{CO}_2$ , Helium (He) was also used as a diluent under  $\text{CO}_2$  starved conditions in order to maintain a temperature less than  $2500^\circ\text{K}$ . Although no laser action was observed, it was confirmed that flash photolysis in excess of 1000J. produced explosive decomposition of  $\text{HN}_3$  and resulted in a 100% increase in pressure from  $\text{HN}_3$ . This result adds some support to the assumptions of the explosion model but does not provide an insight into the reasons for the unobserved laser action.

Of primary importance to laser action is the alignment of the optical cavity. The alignment of the far cavity mirror is certainly within the limits necessary; however, the relatively large diameter hole (2.0 mm.) in the output mirror makes its alignment difficult. In addition the vibrations from the vacuum pump, which was mounted near the laser cavity, adds to the doubt of the necessary accuracy in alignment.

The large amount of energy (37%) extracted by a 2-mm. diameter hole, in addition to the Brewster window and mirror losses (estimated at 2.0%), would preclude laser action if the gain were lower than that predicted by the model. For this reason, two closed mirrors were also used; however, alignment was even more doubtful under this setup since it required alignment on the front of one mirror and the back of the other.



Two additional factors which hampered the detection of laser action were radiation from the triggering circuit and the necessity of storing the laser mixture in the system's only pressure gage. The radiation was on the order of 5 millivolts per centimeter and therefore would only be significant under conditions of small gain. The trigger circuit was redesigned to no avail and finally a pulse generator was ordered; however, delays in delivery prevented its use. The storing of the laser mixture in the pressure gage, however, precluded its use during evacuation of the laser tube after each experiment. The elimination of the products from the laser tube therefore was based on time. However, this is thought to be of minor importance and is easily remedied by the addition of a small pressure sensing device.

The latter problems are of minor importance and correction was only limited by the time required for delivery of the necessary equipment. However, alignment is most critical to the detection of laser action. For this reason it is thought that a beam splitter internal to the resonator cavity should be used for alignment so both mirrors may be closed and aligned at the same time. The most effective method of determination of laser output is that of a gain experiment, and in addition it insures alignment of all components in the system at the same time. The timely repair of the CO<sub>2</sub> laser which was to be used in gain experimentation prevented this type of investigation.





## VIII. CONCLUSIONS AND RECOMMENDATIONS

The major objectives of the research conducted were the analytical modeling and experimental determination of laser action for the  $\text{HN}_3 + \text{CO}_2$  chemical laser. The analytical model has been completed in the form of a computer model which predicts the magnitude and duration of laser gain as well as the population inversion within the laser medium. Experimental observation of laser action has not been accomplished; however, the results obtained indicate difficulties in the experimental setup to be the reason.

The following recommendations are made for possible improvements in the model and experimental investigation:

### A. ANALYTICAL MODEL

1. Experimental determination of the rate constants for reactions b and c.
2. Inclusion of the reactions resulting in the formation of  $\text{NH}_3$ .
3. Expansion of the model to include lasing energy produced and percentage of energy lost due to the experimental setup.

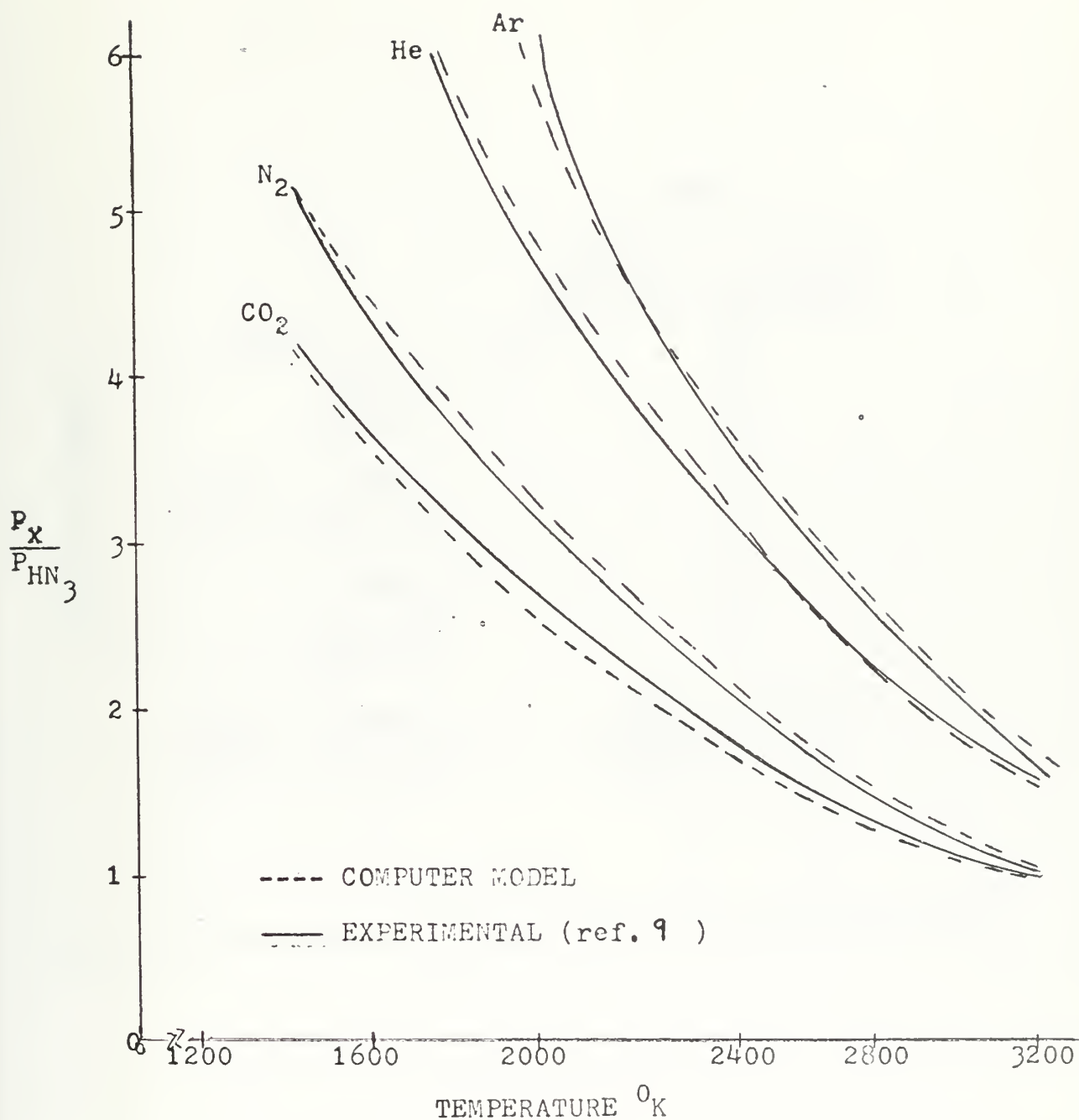
### B. EXPERIMENTAL

1. A gain experiment to determine the existence of laser action.



2. The use of a partial transmitting mirror as part of the laser cavity to reduce the amount of energy removed from the cavity on each pass.
3. Procurement of a Trigger Pulse Generator to reduce the electrical noise picked up by the recording equipment.
4. Inclusion of a storage system for  $\text{HN}_3$  in the experimental setup. This would reduce exposure to the toxic chemicals used to generate  $\text{HN}_3$  to allow more experiments per generation.
5. Extension of the laser cavity to increase the laser gain on each pass through the cavity.
6. The use of a rapid frequency scanner to determine the wavelength of laser action.
7. Operation of the laser tube as a pure  $\text{CO}_2 + \text{N}_2$  laser by high voltage excitation would also provide the necessary alignment information.

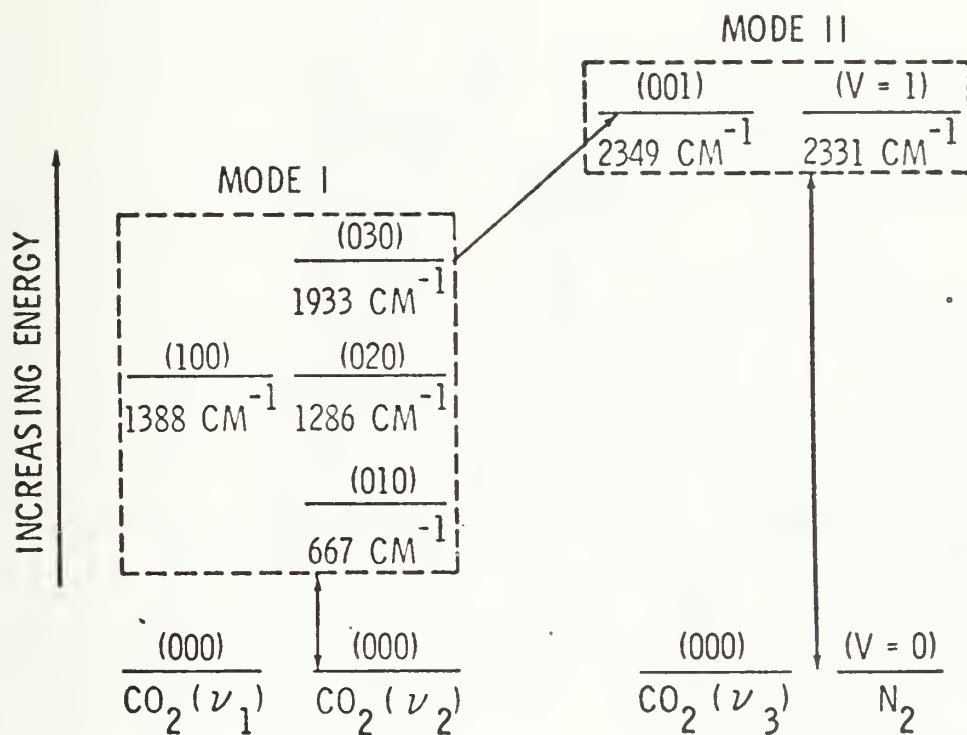




COMPARISON OF THEORETICAL AND EXPERIMENTAL  
ADIABATIC TEMPERATURE FOR VARIOUS DILUTION  
OF  $HN_3$ .

Figure 1 .





SCHEMATIC OF THE GROUPING OF ENERGY LEVELS FOR THE VIBRATIONAL MODEL

Figure 2.





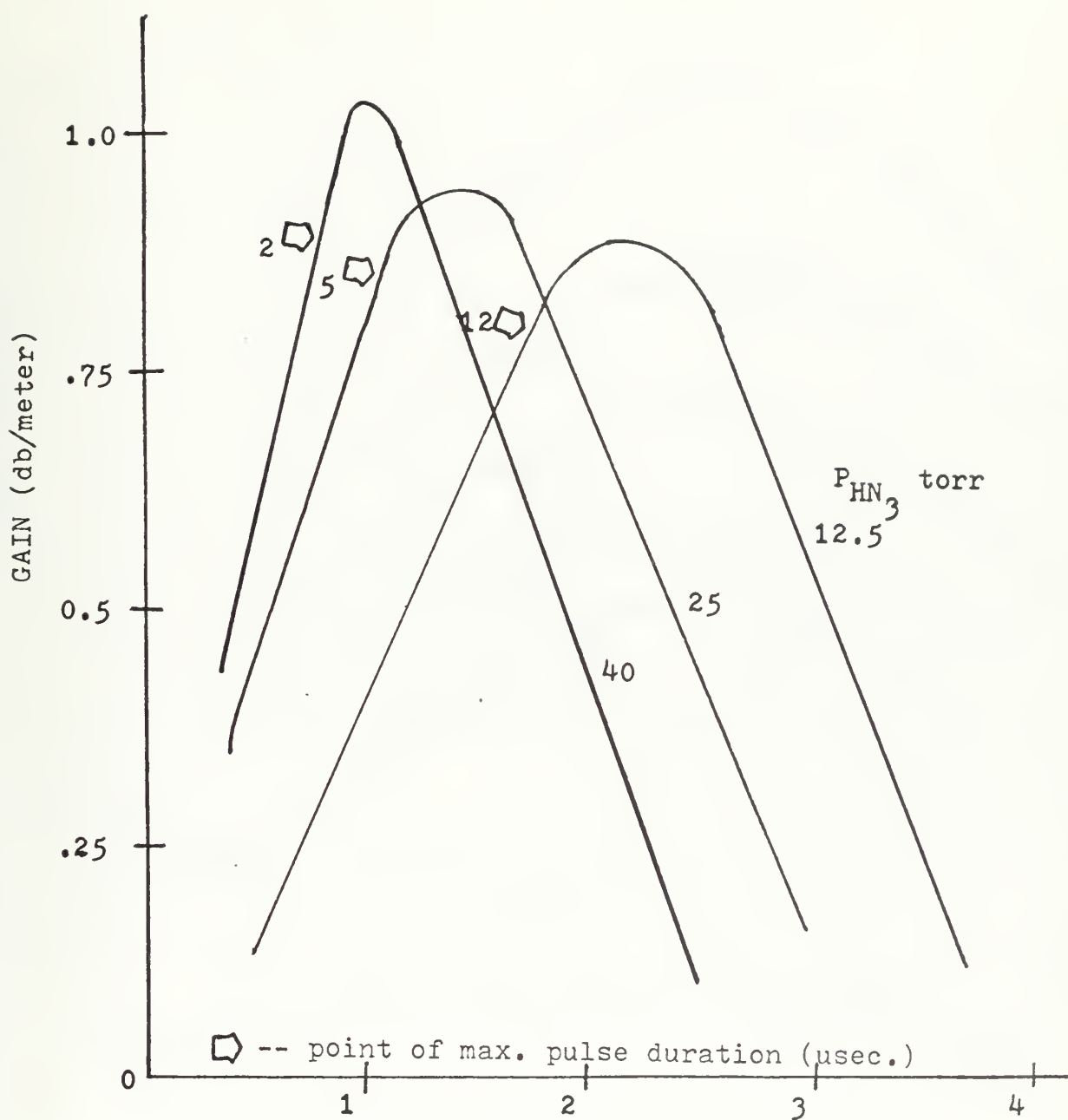


Figure 3. Resulting Gain from dilution of  $\text{HN}_3$  with  $\text{CO}_2$ .



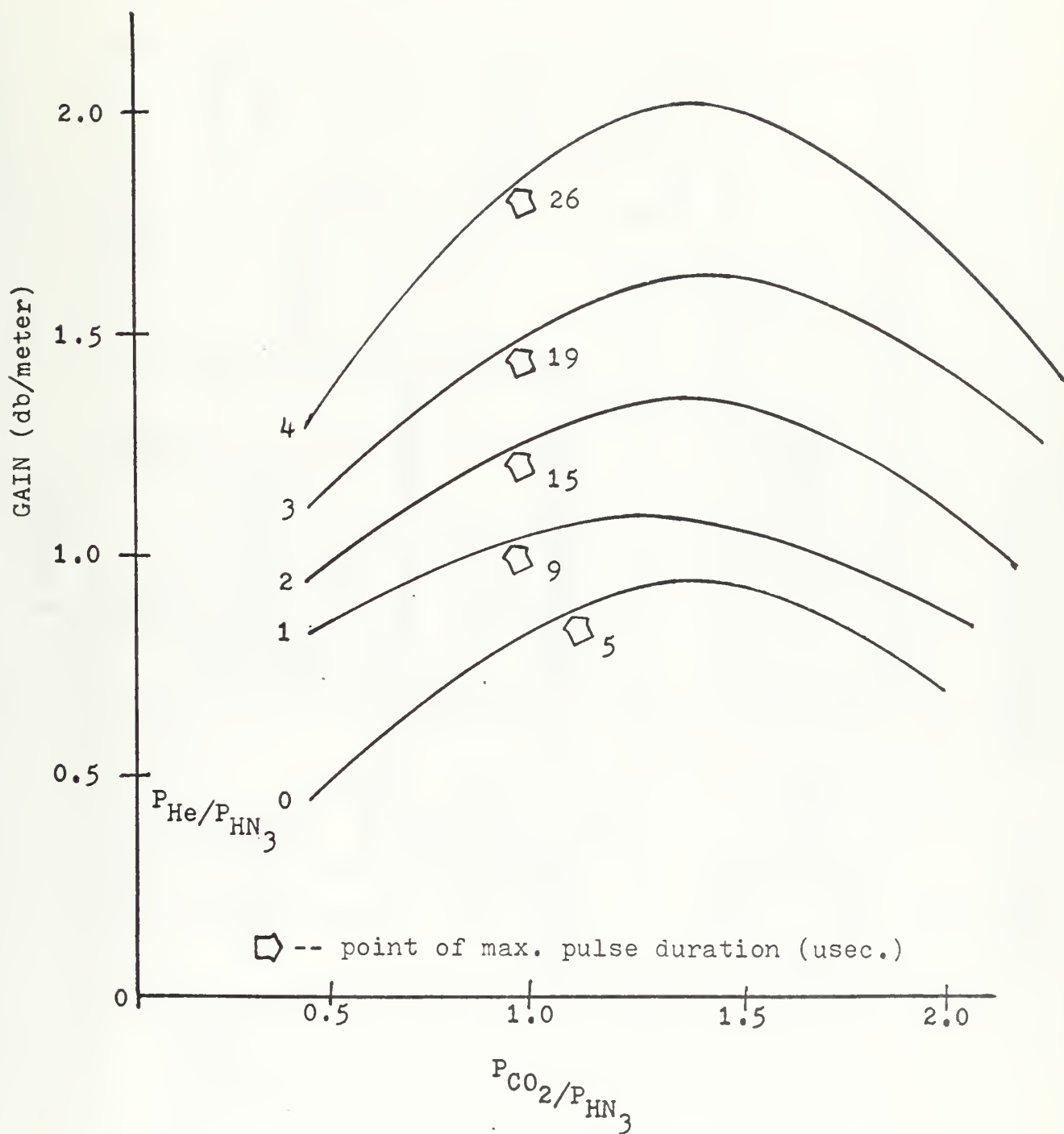


Figure 4. Increase in Gain resulting from the addition of He to an  $HN_3 + CO_2$  mixture.



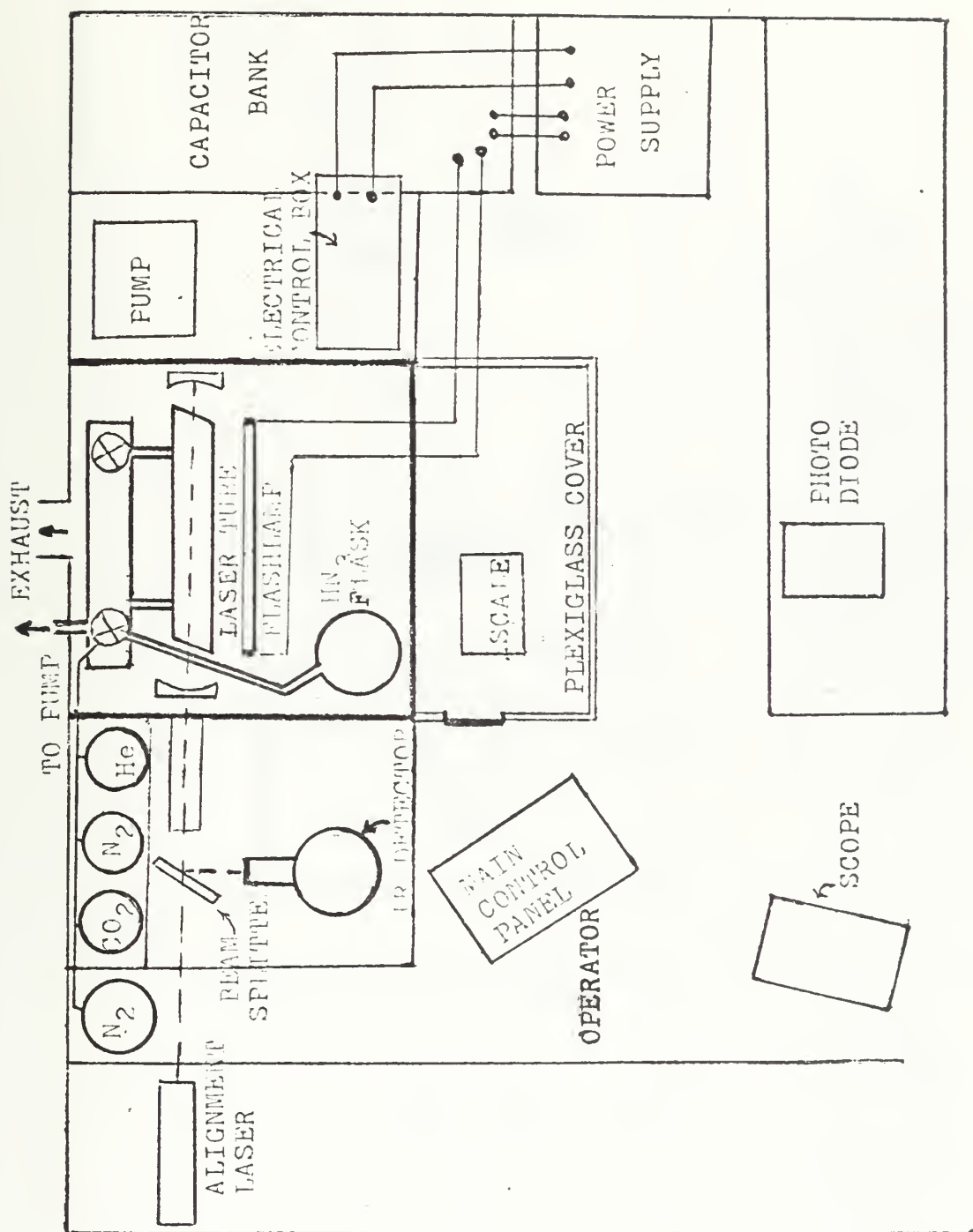
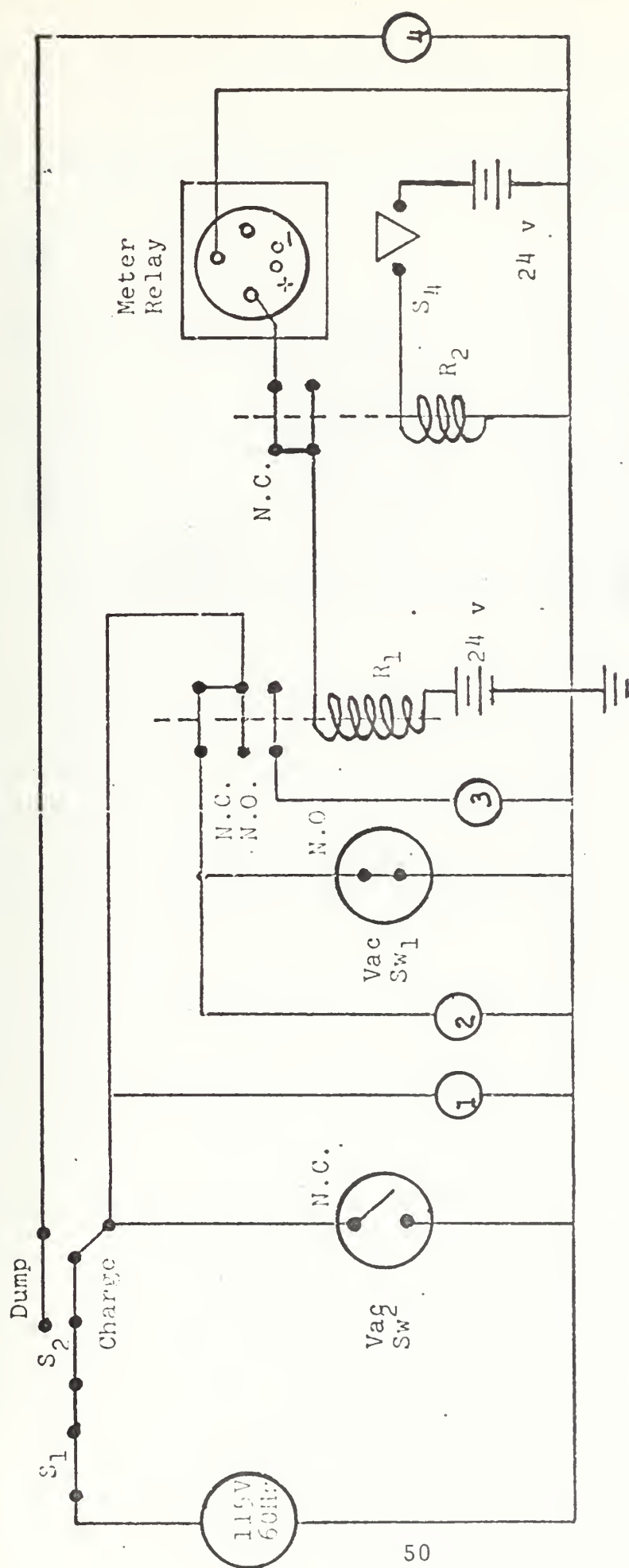


Figure 5 • Experimental Setup





S<sub>1</sub>: On-Off switch  
 S<sub>2</sub>: Door safety interlock  
 S<sub>3</sub>: Charge-Dump switch  
 S<sub>4</sub>: "Fire" push button  
 R<sub>1</sub>, R<sub>2</sub>: 24 v DC Relay

1: Charge warning flasher  
 2: "Charging" indicator light  
 3: "Ready" indicator light  
 4: "Dumped" indicator light  
 N.O.: Normally open  
 N.C.: Normally closed

Figure 6. Schematic of the Electrical Control Box





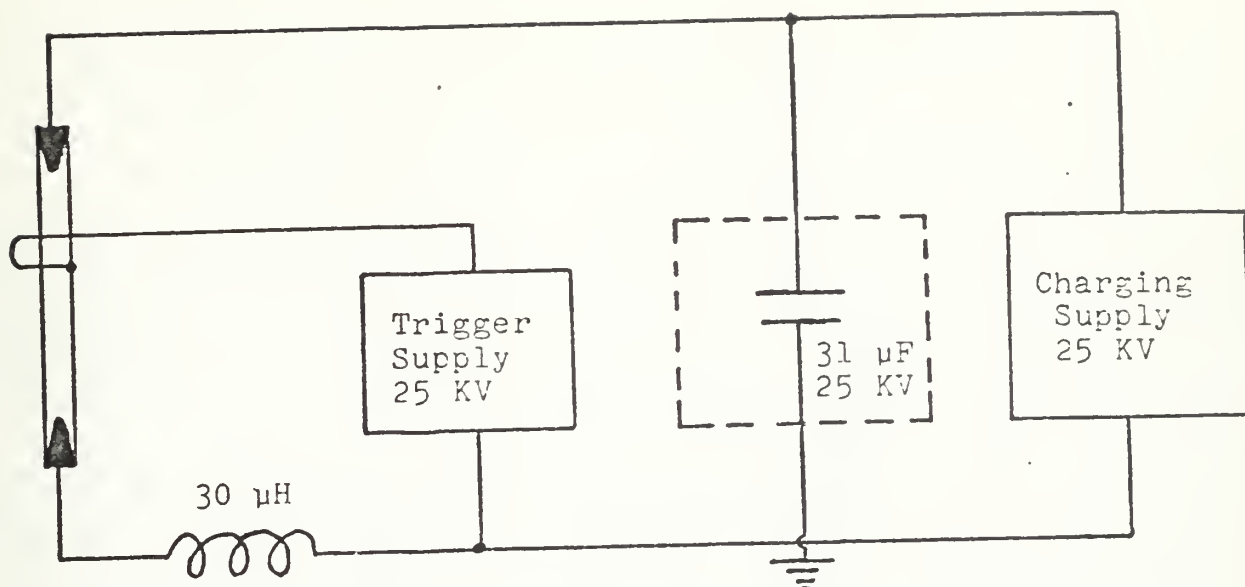


Figure 7 . Flashlamp Discharge Circuit



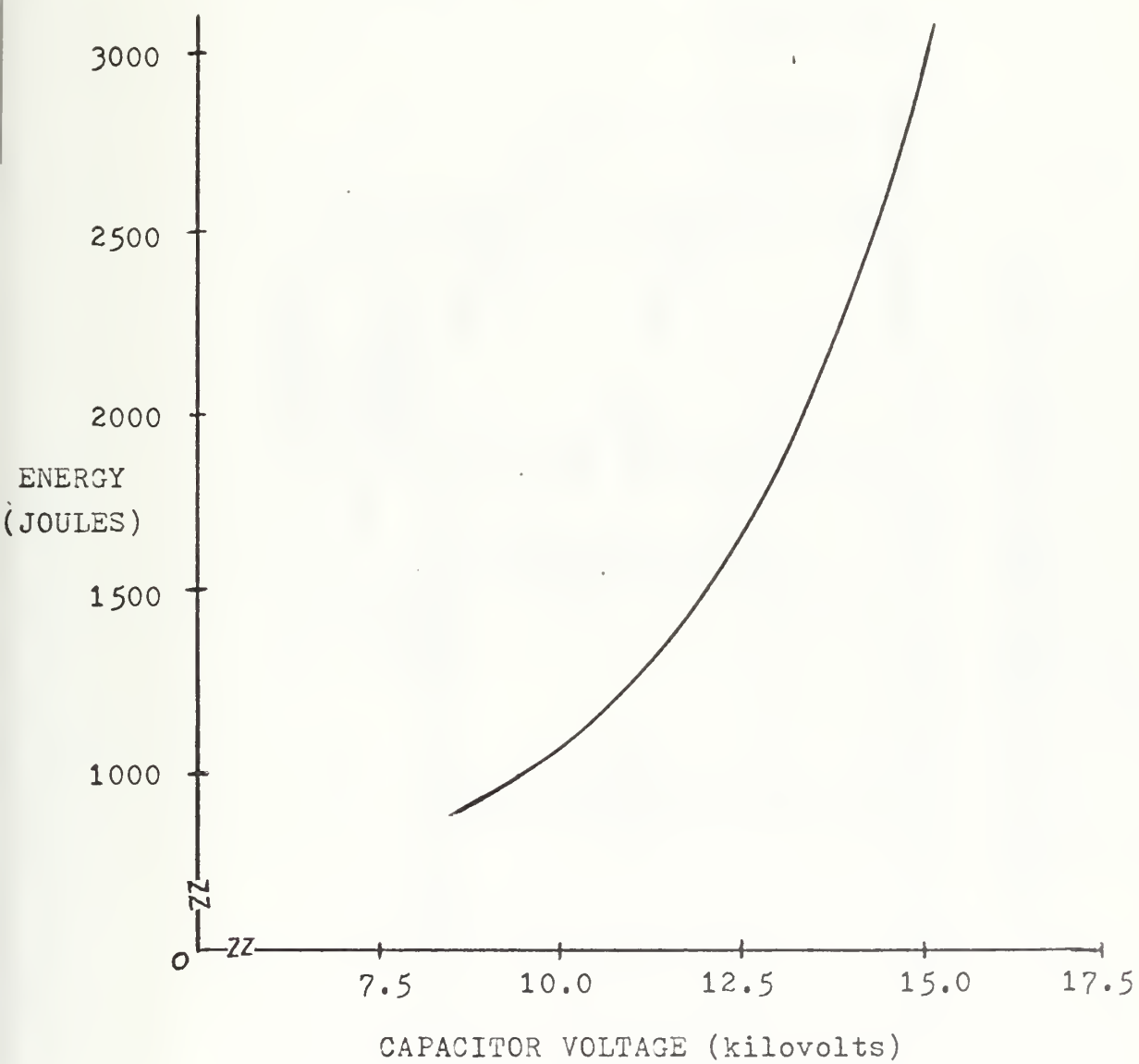


Figure 8 . Flash Energy vs. Capacitor Voltage



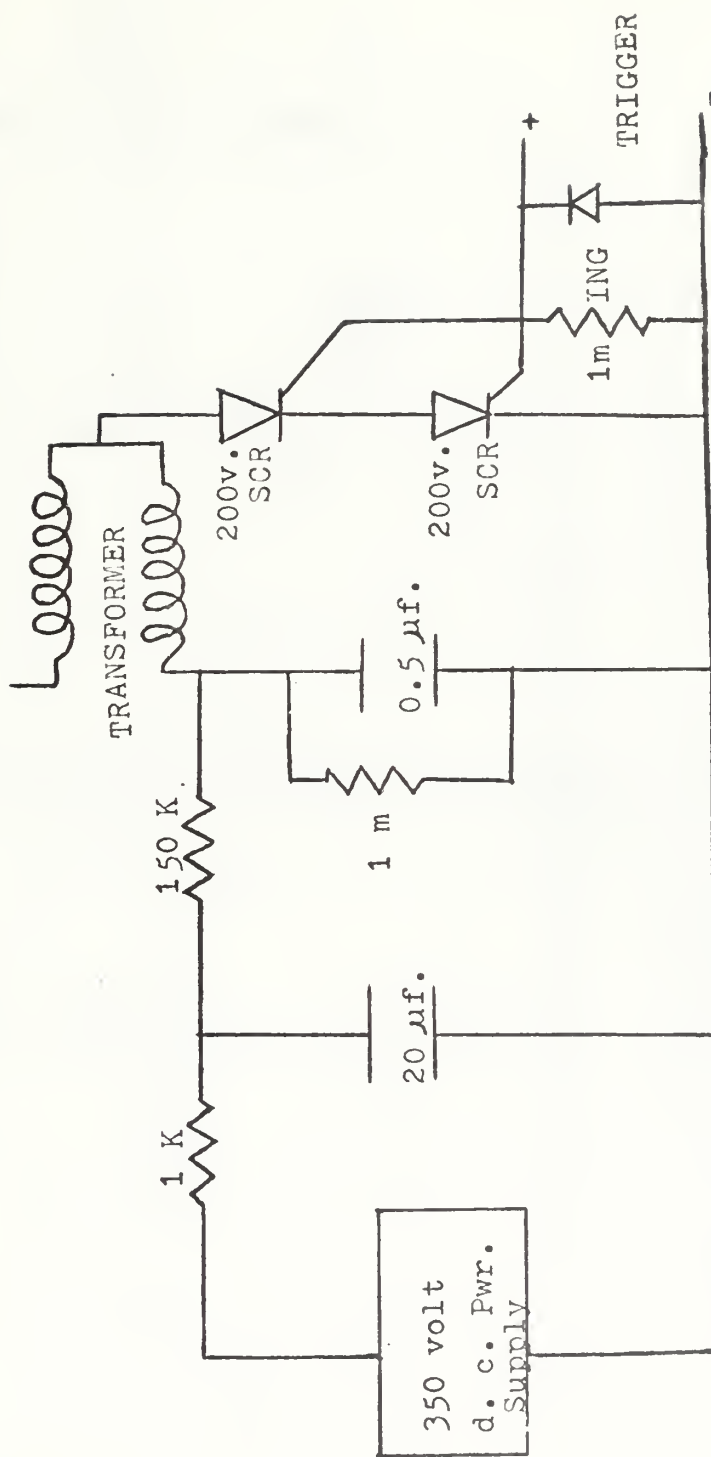


Figure 9. Flash Lamp Trigger Circuit



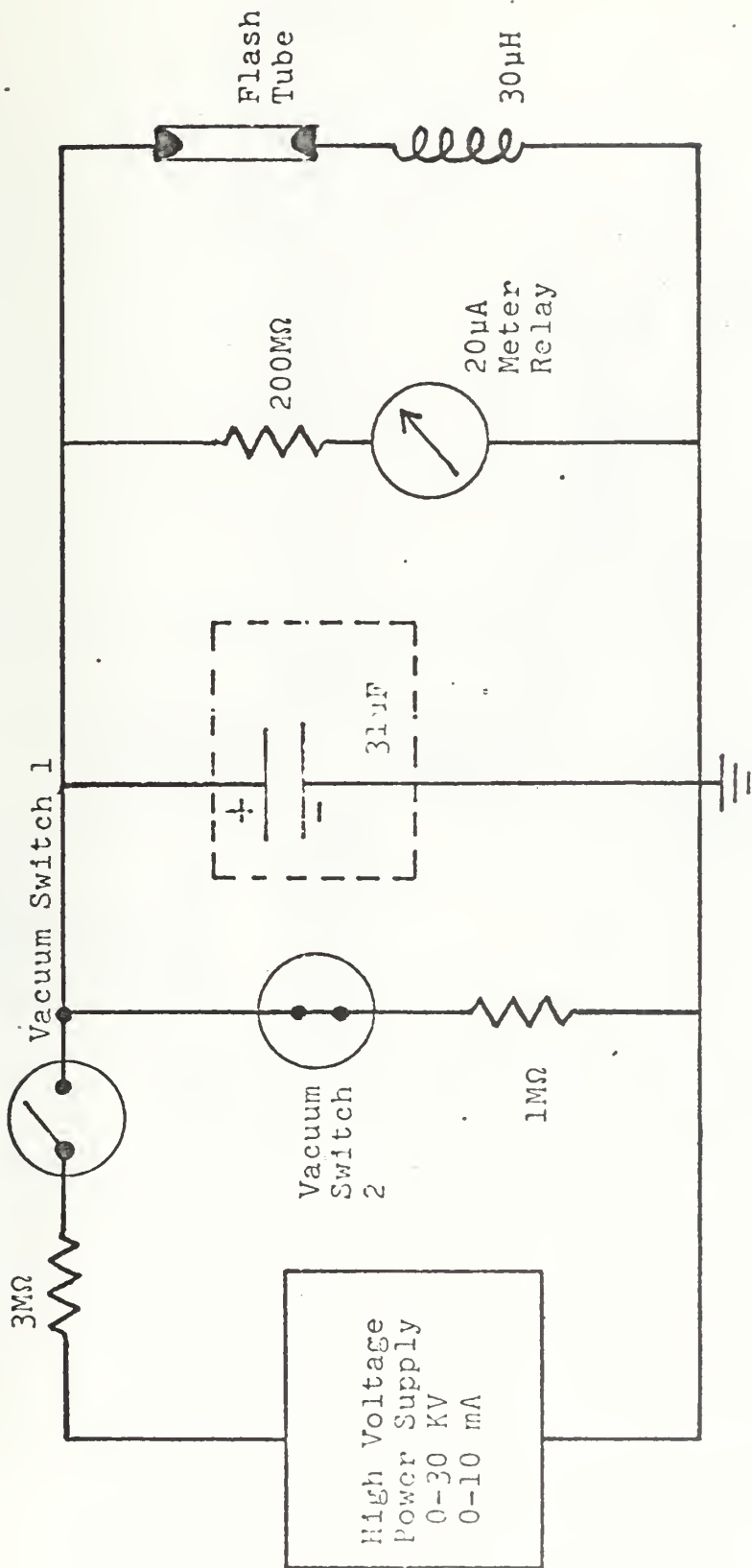
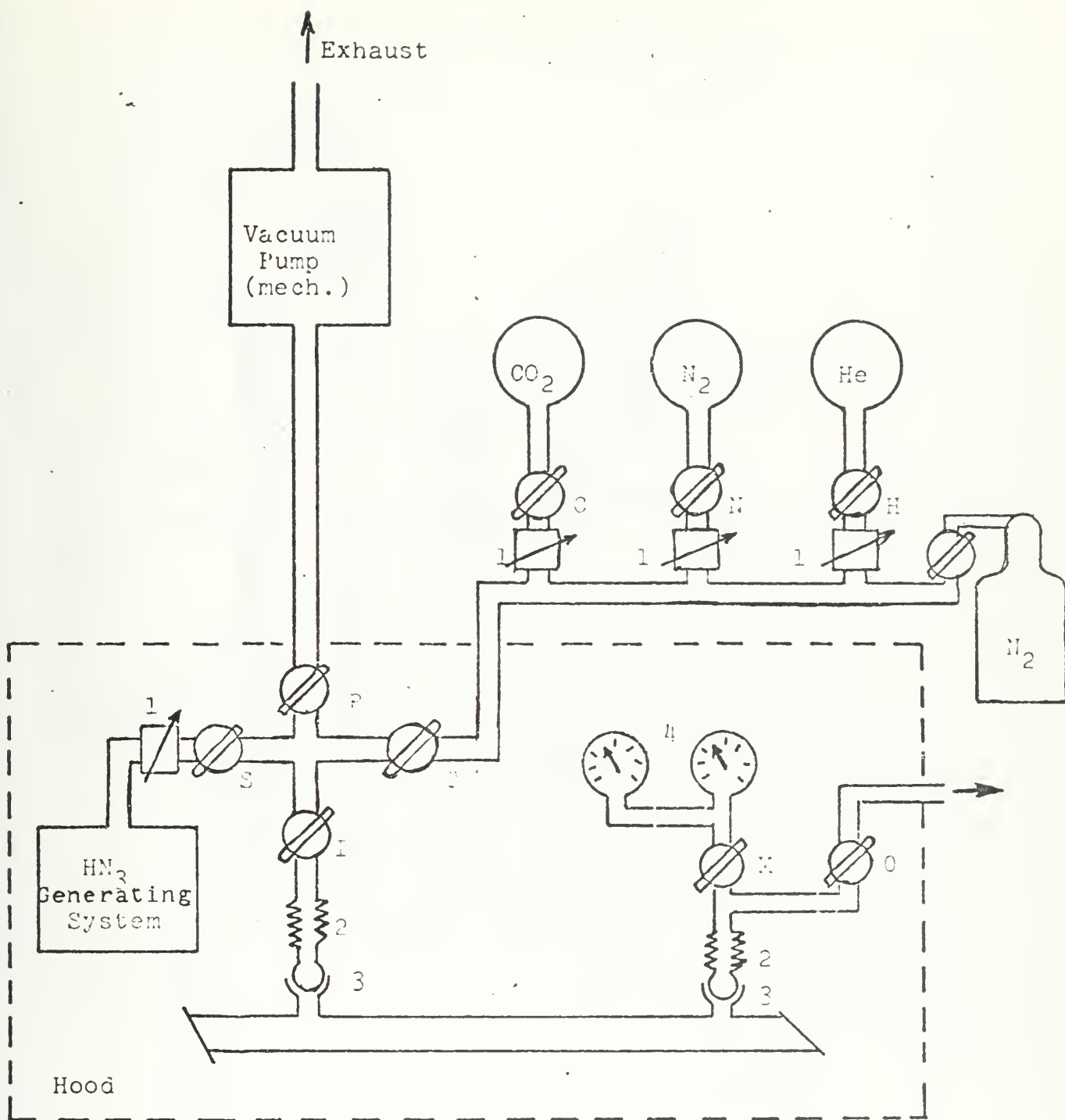


Figure 10. Block Diagram of Charging System.

Vacuum switches 1 and 2 are shown in normal (de-energized) position.







1. Needle valve and bypass
2. Stainless steel bellows
3. Balljoints
4. Bourdon tube and thermocouple gauge

Figure 11. Vacuum System



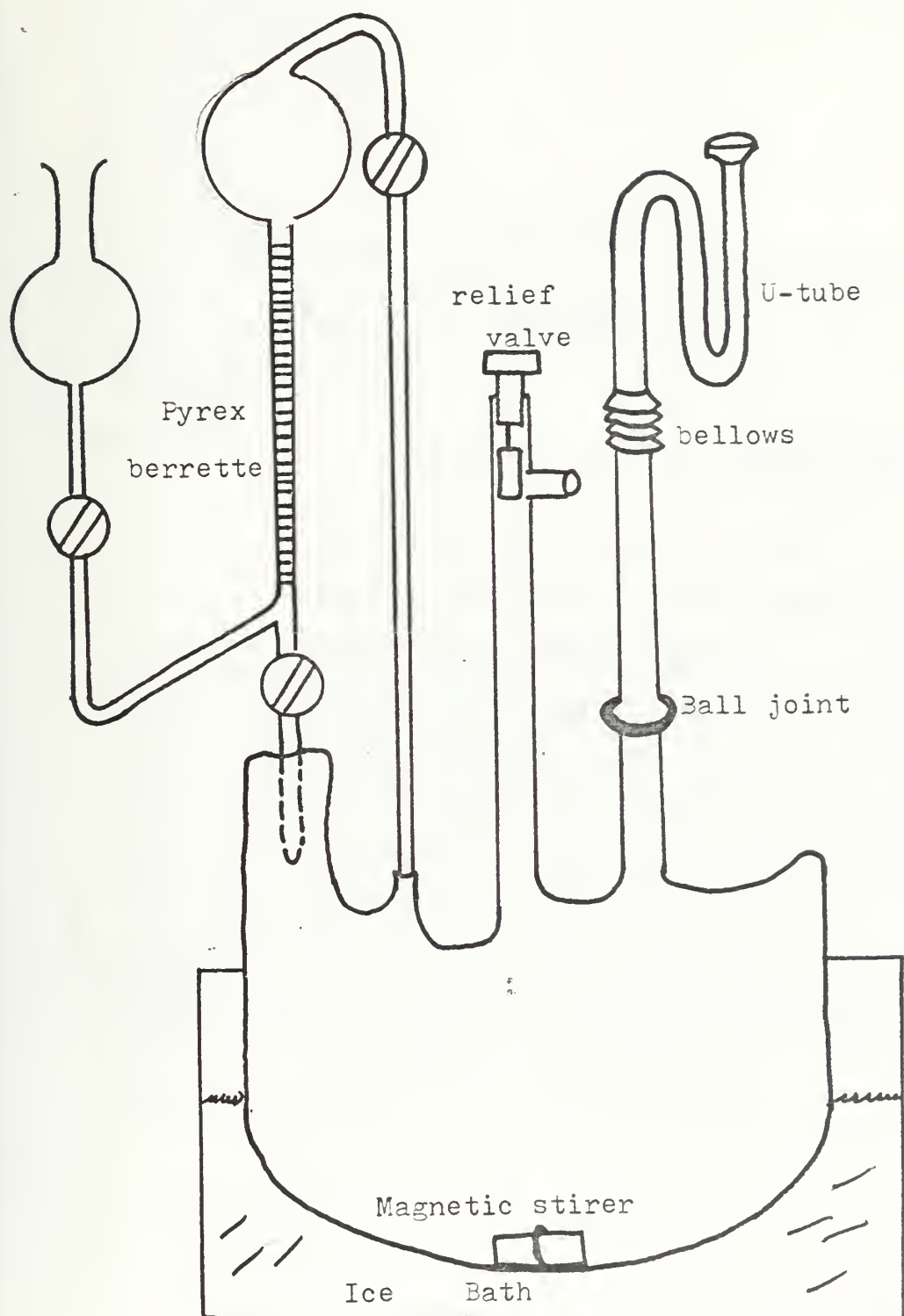


Figure 12.  $\text{HN}_3$  Gas Generator



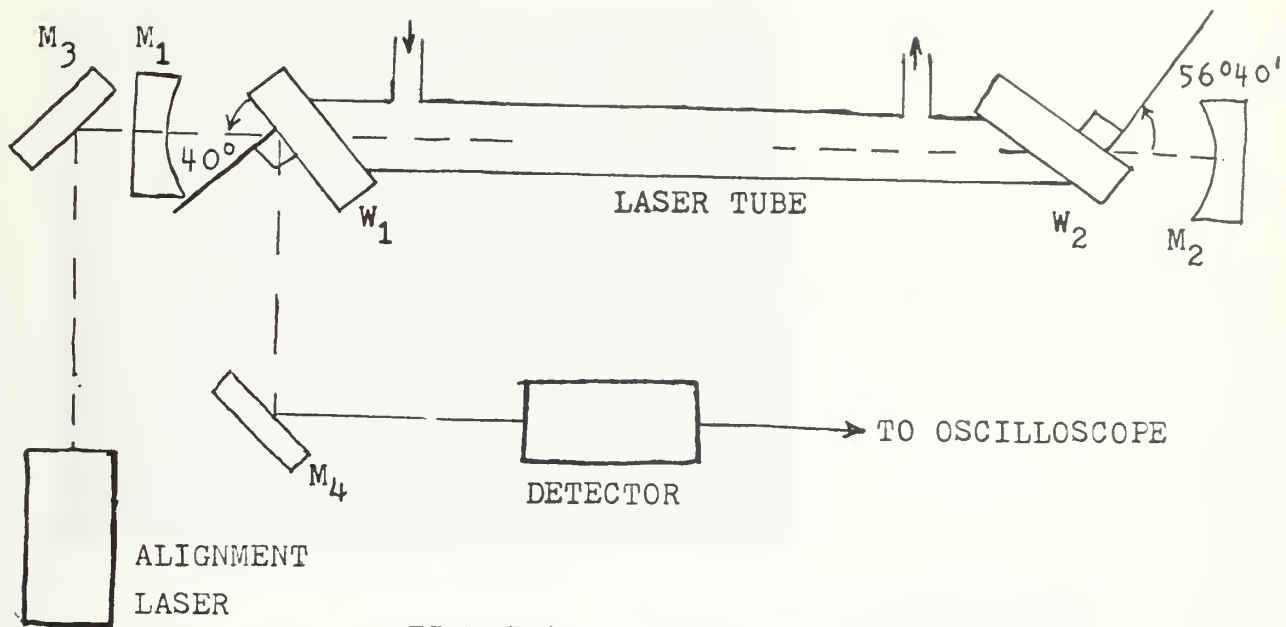


FIGURE 13. Optical System Setup One

$M_1, M_2$ : Concave cavity mirrors

$M_3, M_4$ : Plane front coated mirrors

$W_1, W_2$ : NaCl laser windows

$Y_1$ : NaCl beam splitter

$Z_1$ : 2 mm. hole

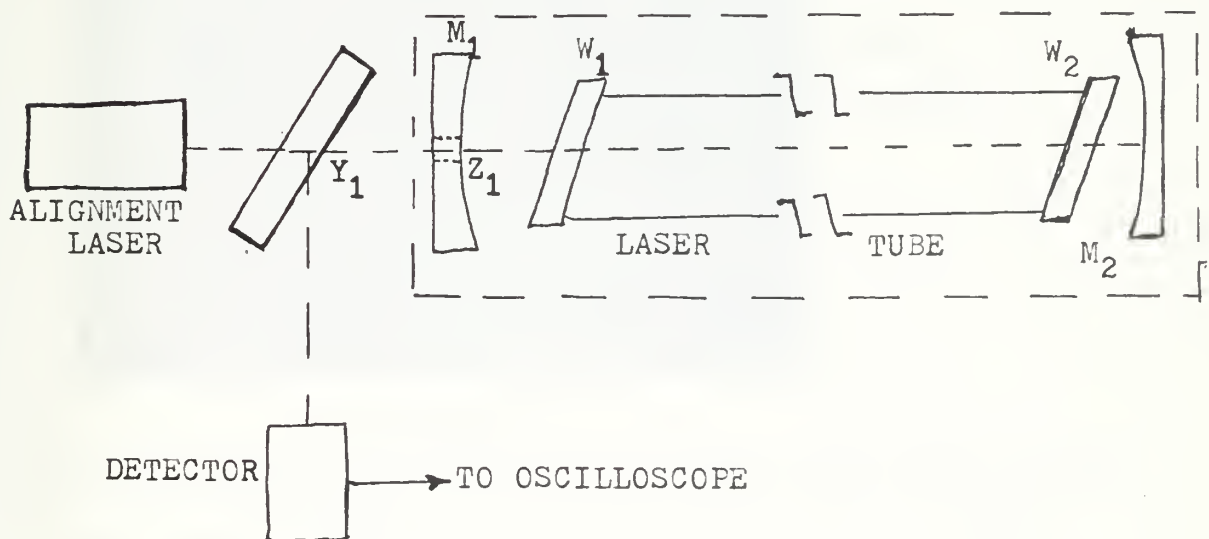


FIGURE 14. Optical System Setup Two



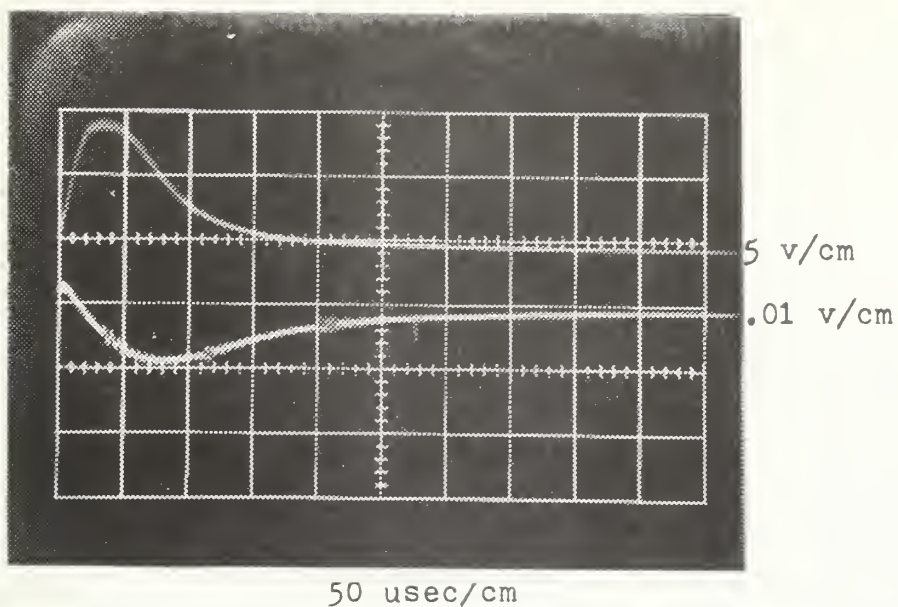


Figure **15**. Oscilloscope trace of output from Photo Diode (upper) and IR Detector with 10.2 filter (lower).

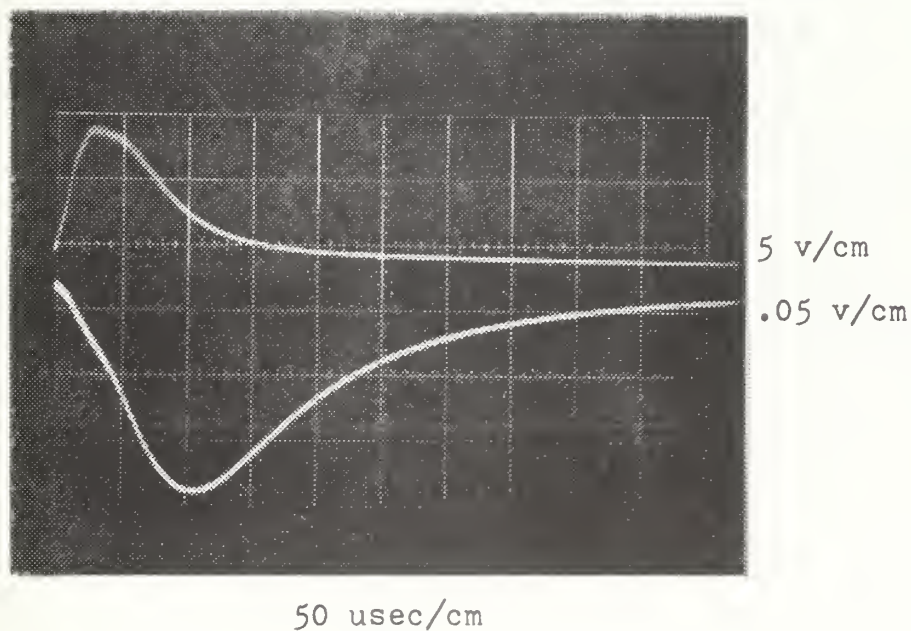


Figure **16**. Oscilloscope trace of output from Photo Diode (upper) and IR Detector with Irtran II filter (lower).





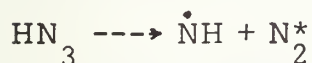
$\text{HN}_3$ torr	$\text{NaN}_3$ grams	$\text{H}_3\text{PO}_4$ grams
10	0.0382	0.0576
20	0.0764	0.1153
30	0.1132	0.1729
40	0.1520	0.2305
50	0.1900	0.2880

TABLE I. Amounts of  $\text{NaN}_3$  and  $\text{H}_3\text{PO}_4$  necessary to generate a desired pressure of  $\text{HN}_3$  in a one liter system.

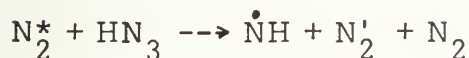


# APPENDIX A: REACTIONS AND RATE CONSTANTS USED IN THE COMPUTER MODEL

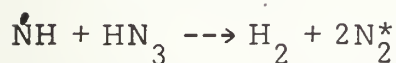
All rate constants are in the units of:  $\text{part.}^{-1} \text{cc.} \cdot \text{sec}^{-1}$



$$\text{KHV} = 2.89 \times 10^{15} t^3 - 6.4 \times 10^{11} t^2 + 3.42 \times 10^7 t$$



$$\text{K2} = 7.64 \times 10^{-9} e^{-6400/\text{RT}}$$

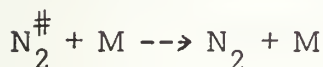


$$\text{K3} = 8.7 \times 10^{-7} e^{-8210/\text{RT}}$$



$$\text{K4} = 3.6 \times 10^{-12} T^{0.55} e^{-1900/\text{RT}}$$

(Ref. 33)



This equation as stated before is only a representation of the reactions that must be considered in the computer model. The following equations are those actually required for each diluent considered.



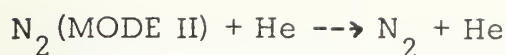
$$\text{K} = e^{-8.76T^{-1/3} - 2.23}$$



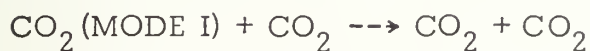
$$\text{K} = e^{-0.0472T^{1/2} - 27.36} \quad \text{for } T \leq 1000^\circ\text{K}$$

$$\text{K} = e^{0.153T^{1/2} - 33.83} \quad \text{for } T \geq 1000^\circ\text{K} \quad (\text{Ref. 29})$$

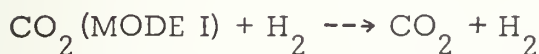




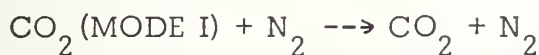
$$K = 1.36 \times 10^{-16} T^{10} (60.7 T^{-1/3} - 4.168) \quad (\text{Ref. 24})$$



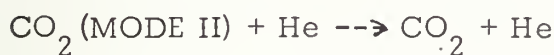
$$K = 1.36 \times 10^{-16} T^{10} (17.8 T^{-1/3} - 1.808) \quad (\text{Ref. 24})$$



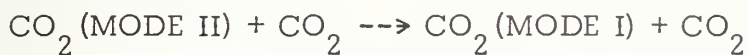
$$K = 4.0 \times 10^{-12} \quad (\text{Ref. 29})$$



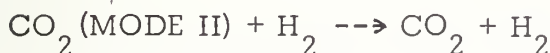
$$K = 3.4 \times 10^{-17} T^{10} (17.8 T^{-1/3} - 1.808) \quad (\text{Ref. 24})$$



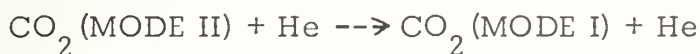
$$K = 3^{-46.23 T^{-1/3} - 23.01} \quad (\text{Ref. 29})$$



$$K = 6.55 \times 10^{-11} T^{-0.1293} \quad (\text{Ref. 29})$$



$$K = 5.0 \times 10^{-14} \quad (\text{Ref. 29})$$



$$K = 5.895 \times 10^{-11} T^{-0.1293} \quad (\text{Ref. 24})$$



$$K = 1.36 \times 10^{-17.808 - 17.8 T^{-1/3}} \quad (\text{Ref. 24})$$





$$K = 6.55 \times 10^{-11} T^{-0.1293} e^{-1431.5/T_{\text{vib}}}$$

(Ref. 24)





APPENDIX B:  $\text{HN}_3 + \text{CO}_2$  LASER PROGRAM

CCCCCCCCCCCC

APPENDIX B:  $\text{HN}_3 + \text{CO}_2$  LASER PROGRAM

THIS PROGRAM CALCULATES THE POPULATION INVERSION

AND LASER GAIN PRODUCED WITHIN  $\text{CO}_2$

IMPLICIT REAL\*8 (A-H,K,O-Z)  
REAL\*4 XGPH,YGPH,T,G0,G2,G9  
DIMENSION F(17),Y(17),XGPH( 200),YGPH( 200),T(200)  
1,G2(200),G9(200),R(10,10)

CC

MOLAR GAS CONSTANT

RO=62361.0

STEP SIZE

H=1.0D-08

N=17 NO. OF EQUATIONS TO BE INTEGRATED

INITIAL TIME

X=0.0D0

THETA V OF THE FIRST VIBRATIONAL LEVEL OF N2

HN1=-3354.301991

LOSCHMIDT'S NUMBER

AL=2.6874D19

AVOGADRO'S NUMBER

AN=6.0254D23

INITIAL VALUES FOR CONTROL OF OUTPUT AND INTEGRATION

M=1

MM=1

NN=1

I=1

JJ=1

NT=0

U=0.0

G0=0.0D0

CCCCCCCCCCCC

INITIAL CONCENTRATIONS OF REACTANTS

Y(1)--HN3

Y(2)--HN

Y(3)--H2

00000010  
00000020  
00000030  
00000040  
00000050  
00000060  
00000070  
00000080  
00000090  
00000100  
00000110  
00000120  
00000130  
00000140  
00000150  
00000160  
00000170  
00000180  
00000190  
00000200  
00000210  
00000220  
00000230  
00000240  
00000250  
00000260  
00000270  
00000280  
00000290  
00000300  
00000310  
00000320  
00000330  
00000340  
00000350  
00000360  
00000370  
00000380  
00000390  
00000400  
00000410  
00000420  
00000430  
00000440  
00000450  
00000460  
00000470  
00000480



```

000000490
000000500
000000510
000000520
000000530
000000540
000000550
000000560
000000570
000000580
000000590
000000600
000000610
000000620
000000630
000000640
000000650
000000660
000000670
000000680
000000690
000000700
000000710
000000720
000000730
000000740
000000750
000000760
000000770
000000780
000000790
000000800
000000810
000000820
000000830
000000840
000000850
000000860
000000870
000000880
000000890
000000900
000000910
000000920
000000930
000000940
000000950
000000960

Y(4)--N2 (GND. LEVEL)
Y(5)...Y(13)---N2 (V=1...9,LEVEL)
Y(14)= CO2 GND STATE
Y(15)= CO2 MODE II (V=1 & V=2 LEVELS)
Y(16)= CO2 MODE I (V=3 LEVEL)
Y(17)--TEMP.

DO 1 M=1,N
Y(M)=0.000
CONTINUE
Y(17)=300.0
Y(1)=(25.00/(RO*Y(17)))*AN
Y(14)=( 12.50/(RO*Y(17)))*AN
HE=(100.0/(RO*Y(17)))*AN
CO2= TOTAL CONC. OF CARBON DIOXIDE
CO2=Y(14)
VIBRATIONAL TEM. OF N2
VIBRATIONAL TEM. OF N2 (V=0,1)
TV=Y(17)
WRITE (6,101)
WRITE (6,102)U,Y(17),Y(1),Y(2),Y(4),Y(5),Y(14),Y(15),Y(16),GO
INITIALIZE THE MATRIX FOR THE TRANSION PROBABILITIES
OF PURE N2
DO 6 L=1,10
DO 6 LL=1,10
6 R(L,LL)=0.000

OUTSIDE DO LOOP FOR INTEGRATION OF THE RATE EQ.'S
22 FT=0.0

SPECIFIC HEAT AT CONSTANT VOLUME
FOR H2
CVH=5.76+5.78D-04*1.8*Y(17)+(20.0/(1.8*Y(17)))*0.5D0)-1.987
FOR CO2
CVC=16.1-(6530.0/(1.8*Y(17)))+(1.41D06/(1.8*Y(17))**2)-1.987
FOR N2
CVN=9.47-(3470.0/(1.8*Y(17)))+(1.16D06/(1.8*Y(17))**2)-1.987
IF(Y(17).GT.2500.0) CVH=CVN
CALCULATE THE TOTAL CONC. OF N2

```







```

C      K11=K6/0.27D0
C      C02(NI) + HE ---> C02 + HE
C      K12=DEXP(-46.22873949D0*Y(17)**(-1.0D0/3.0D0)-23.00814718)
C      N2(V=1) + HE ---> N2 + HE
C      K13=Y(17)*1.0D06/(10.0D0**((60.7*Y(17)**(-1.0D0/3.0D0))-4.168)
C      1*AL*273.0)
C      C02 + C02 ---> C02 + C02(NI)
C      K14=K9*DEXP(-960.0/Y(17))
C      C02 + C02(NI) ---> C02 + C02(NII)
C      K15=K11*DEXP(-1431.5/TV)
C      TRANSITIONS PROBABILITIES FOR N2 VIB LEVELS
C      R(2,1)=(AL*273.0/Y(17))*DEXP(-290.457*Y(17)**(-1.0/3.0)-12.5062)
C      IF(Y(17).GT.1953.0) R(2,1)=(AL*273.0/Y(17))*DEXP(-56.6866*
C      1Y(17)**(-1.0/3.0)-31.20782)
C      IF(Y(5).LT.10.0) GO TO 11
C      CAL. OF THE VIBRATIONAL TEMP. OF N2
C      TV=HNV1/DLOG(Y(5)/Y(4))
C      IF(TV.LT.Y(17)) TV=Y(17)
C      11 R(1,2)=R(2,1)*DEXP(HNV1/TV)
C      DO 5 LL=2,9
C      R(LL+1,LL)=DFLOAT(LL)*9.6544D03*DSQRT(Y(17))
C      R(LL,LL+1)=R(LL+1,LL)*DEXP(HNV1/TV)
C      5 CONTINUE
C      RATE EQ'S. FOR Y(1)...Y(17)
C      F(1)=-K1*Y(1)*Y(13)-K2*Y(2)*Y(1)-KHV*Y(1)
C      F(2)=K1*Y(1)*Y(13)-K2*Y(2)*Y(1)-KHV*Y(1)
C      1-K3*2.C*Y(2)*Y(2)+KHV*Y(1)
C      F(3)=K2*Y(2)*Y(1)+K3*Y(2)*Y(2)
C      F(13)=-K1*Y(13)*Y(1)+K2*2.0*Y(2)*Y(1)+KHV*Y(1)-R(10,9)*Y(13)
C      1+R(9,10)*Y(12)
C      F(4)=K1*Y(13)*Y(1)+K4*Y(5)*Y(3)
C      1+R(2,1)*Y(5)-R(1,2)*Y(4)-K5*Y(16)*Y(14)*Y(5)
C      2+K13*Y(5)*HE
C      F(5)=R(1,2)*Y(4)+R(3,2)*Y(6)-R(2,3)*Y(5)-R(2,1)*Y(5)+K1*Y(13)*Y(1)
C      1-K4*Y(5)*Y(3)-K5*Y(14)*Y(5)+K5*Y(16)*Y(4)-K13*Y(5)*HE+K3*Y(2)*Y(2)
C      DO 3 L=3,9
C      F(L+3)=R(L-1,L)*Y(L+2)+R(L+1,L)*Y(L+4)-R(L,L-1)*Y(L+3)
C      1-R(L,L+1)*Y(L+3)
C      3 CONTINUE
C      F(14)=K5*Y(16)*Y(4)+K8*Y(15)*Y(3)+K9*Y(15)*Y(14)-K14*Y(14)**2
C      00001450
C      00001460
C      00001470
C      00001480
C      00001490
C      00001500
C      00001510
C      00001520
C      00001530
C      00001540
C      00001550
C      00001560
C      00001570
C      00001580
C      00001590
C      00001600
C      00001610
C      00001620
C      00001630
C      00001640
C      00001650
C      00001660
C      00001670
C      00001680
C      00001690
C      00001700
C      00001710
C      00001720
C      00001730
C      00001740
C      00001750
C      00001760
C      00001770
C      00001780
C      00001790
C      00001800
C      00001810
C      00001820
C      00001830
C      00001840
C      00001850
C      00001860
C      00001870
C      00001880
C      00001890
C      00001900
C      00001910
C      00001920

```









```

00002410
00002420
00002430
00002440
00002450
00002460
00002470
00002480
00002490
00002500
00002510
00002520
00002530
00002540
00002550
00002560
00002570
00002580
00002590

```

```

14 I=I+1
   IF(X.GT.3.0D-03) GO TO 99
   IF(JJ.LT.201) GO TO 22
C
C   CALL PLOT SUBROUTINE
C
   WRITE(6,103)
   CALL PLOTIP(XGPH,YGPH,200,0)
   WRITE(6,103)
   CALL PLOTIP(XGPH,G2,200,0)
   WRITE(6,103)
   CALL PLOTIP(XGPH,T,200,0)
   FORMAT(1,6X,TIME USEC,3X,TEMP, K,7X,HN3,10X,
101 1,HN,10X,N2,9X,N2 (V=1),8X,CO2,6X,CC2 MODE I,
2 3X,CO2 MODE II,6X,GAIN,/)
102 FORMAT(1,2F13.2,7D13.2,1F13.2)
103 FORMAT(1,/,/)
99 STOP
END

```



CCCCCCCCCCCC

# RKLD EQ INTEGRATING SUBROUTINE

```

DOUBLE PRECISION FUNCTION RKLD EQ (N,Y,F,X,H,NT)
REAL*8 Y,F,X,H,Q,H1,H2,H3,H6
DIMENSION Y(N), F(N), Q(25)
NT = NT + 1
GO TO (1,2,3,4),NT
1 H1 = H1 * .5D0
H3 = H1*2.0D0
H6 = H1/6.0D0
DO 11 J = 1,N
11 Q(J) = 0.0D0
A = .5D0
X = X + H2
GO TO 5
2 A = .292893218813452
GO TO 5
3 A = 1.707106781186547
X = X + H2
GO TO 5
4 DO 41 I = 1,N
41 Y(I) = Y(I) + H6 * F(I) -Q(I)/3.0D0
RKLD EQ = 2.
GO TO 6
5 DO 51 L = 1,N
51 Y(L) = Y(L) + A*(H * F(L) -Q(L))
Q(L) = H3 * A *F(L) +(1.0D0-3.0D0*A) *Q(L)
6 RETURN
END

```

00002600  
00002610  
00002620  
00002630  
00002640  
00002650  
00002660  
00002670  
00002680  
00002690  
00002700  
00002710  
00002720  
00002730  
00002740  
00002750  
00002760  
00002770  
00002780  
00002790  
00002800  
00002810  
00002820  
00002830  
00002840  
00002850  
00002860  
00002870  
00002880  
00002890  
00002900  
00002910  
00002920  
00002930  
00002940  
00002950  
00002960  
00002970  
00002980  
00002990  
00003000  
00003010



## COMPUTER PROGRAM OUTPUT

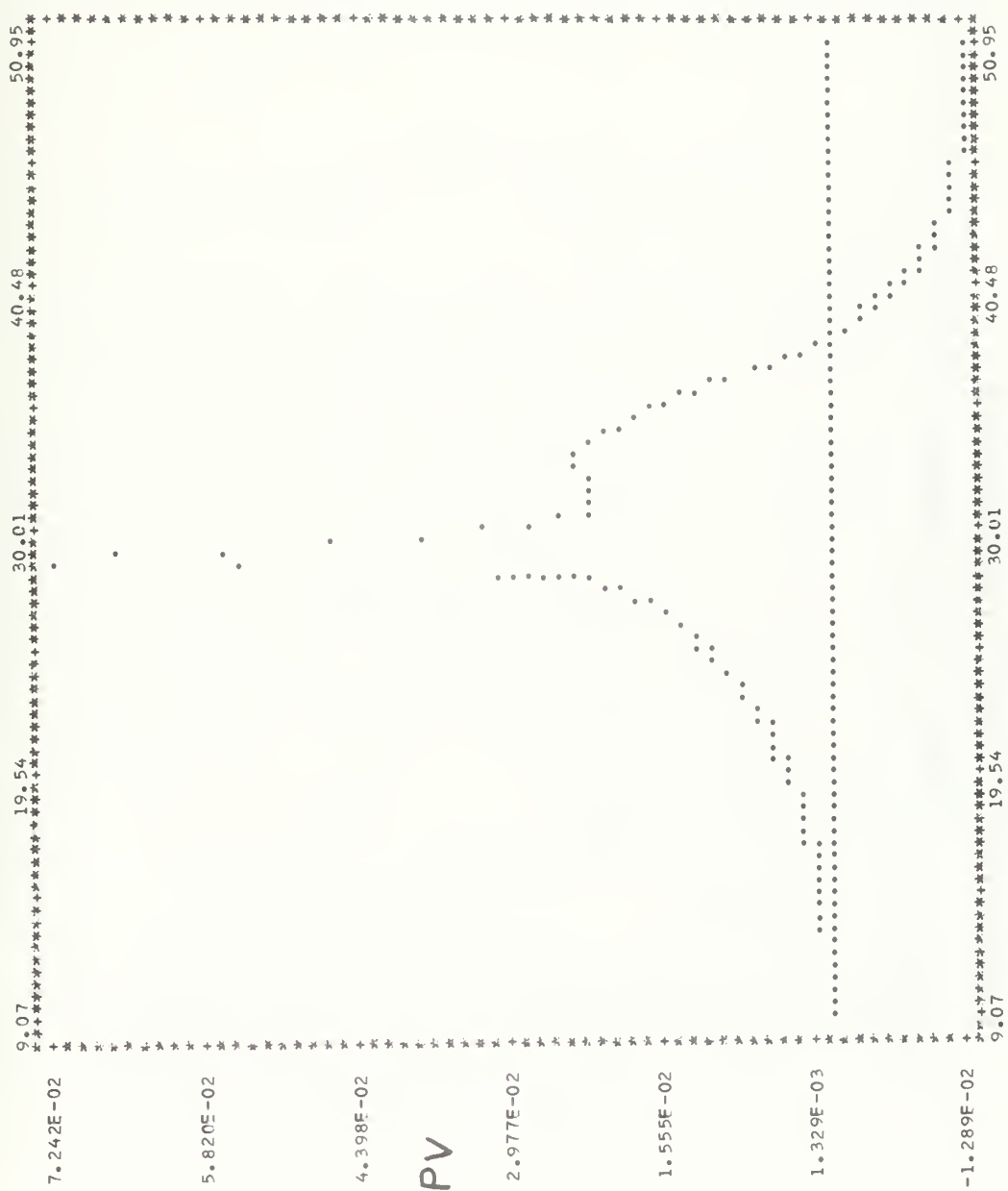
[illegible]





TIME	USEC	TEMP.	K	HN3	HN	N2	N2 (V=1)	CO2	CO2 MODE I	CO2 MODE II	GAIN
1	1	594	67	660	160	780	77	390	700	10	78
2	2	614	63	650	170	830	77	390	710	77	79
3	3	629	58	640	190	900	77	390	720	77	80
4	4	645	53	580	230	1270	88	390	730	77	81
5	5	660	48	490	240	1300	88	390	760	77	82
6	6	676	43	420	250	1410	88	390	800	77	83
7	7	692	38	350	260	1420	88	390	820	77	84
8	8	708	33	290	270	1490	88	390	840	77	85
9	9	724	28	210	280	1520	88	390	870	77	86
10	10	740	23	160	290	1590	88	390	880	77	87
11	11	756	18	110	300	1620	88	390	890	77	88
12	12	772	13	60	310	1690	88	390	900	77	89
13	13	788	8	10	320	1720	88	390	910	77	90
14	14	804	3	0	330	1790	88	390	920	77	91
15	15	820	0	0	340	1830	88	390	930	77	92
16	16	836	0	0	350	1860	88	390	940	77	93
17	17	852	0	0	360	1890	88	390	950	77	94
18	18	868	0	0	370	1900	88	390	960	77	95
19	19	884	0	0	370	1970	88	390	970	77	96
20	20	900	0	0	380	1990	88	390	980	77	97
21	21	916	0	0	380	2000	88	390	990	77	98
22	22	932	0	0	380	2030	88	390	1000	77	99
23	23	948	0	0	390	2060	88	390	1010	77	100
24	24	964	0	0	390	2070	88	390	1020	77	101
25	25	980	0	0	390	2100	88	390	1030	77	102
26	26	996	0	0	390	2110	88	390	1040	77	103
27	27	1012	0	0	390	2120	88	390	1050	77	104
28	28	1028	0	0	390	2130	88	390	1060	77	105
29	29	1044	0	0	390	2140	88	390	1070	77	106
30	30	1060	0	0	390	2150	88	390	1080	77	107
31	31	1076	0	0	390	2160	88	390	1090	77	108
32	32	1092	0	0	390	2170	88	390	1100	77	109
33	33	1108	0	0	390	2180	88	390	1110	77	110
34	34	1124	0	0	390	2190	88	390	1120	77	111
35	35	1140	0	0	390	2200	88	390	1130	77	112
36	36	1156	0	0	390	2210	88	390	1140	77	113
37	37	1172	0	0	390	2220	88	390	1150	77	114
38	38	1188	0	0	390	2230	88	390	1160	77	115
39	39	1204	0	0	390	2240	88	390	1170	77	116
40	40	1220	0	0	390	2250	88	390	1180	77	117
41	41	1236	0	0	390	2260	88	390	1190	77	118
42	42	1252	0	0	390	2270	88	390	1200	77	119
43	43	1268	0	0	390	2280	88	390	1210	77	120
44	44	1284	0	0	390	2290	88	390	1220	77	121
45	45	1300	0	0	390	2300	88	390	1230	77	122
46	46	1316	0	0	390	2310	88	390	1240	77	123
47	47	1332	0	0	390	2320	88	390	1250	77	124
48	48	1348	0	0	390	2330	88	390	1260	77	125
49	49	1364	0	0	390	2340	88	390	1270	77	126
50	50	1380	0	0	390	2350	88	390	1280	77	127
51	51	1396	0	0	390	2360	88	390	1290	77	128
52	52	1412	0	0	390	2370	88	390	1300	77	129
53	53	1428	0	0	390	2380	88	390	1310	77	130
54	54	1444	0	0	390	2390	88	390	1320	77	131
55	55	1460	0	0	390	2400	88	390	1330	77	132
56	56	1476	0	0	390	2410	88	390	1340	77	133
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63	63	1588	0	0	390	2480	88	390	1410	77	140
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129	129	2644	0	0	390	3140	88	390	2070	77	206
130	130	2660	0								





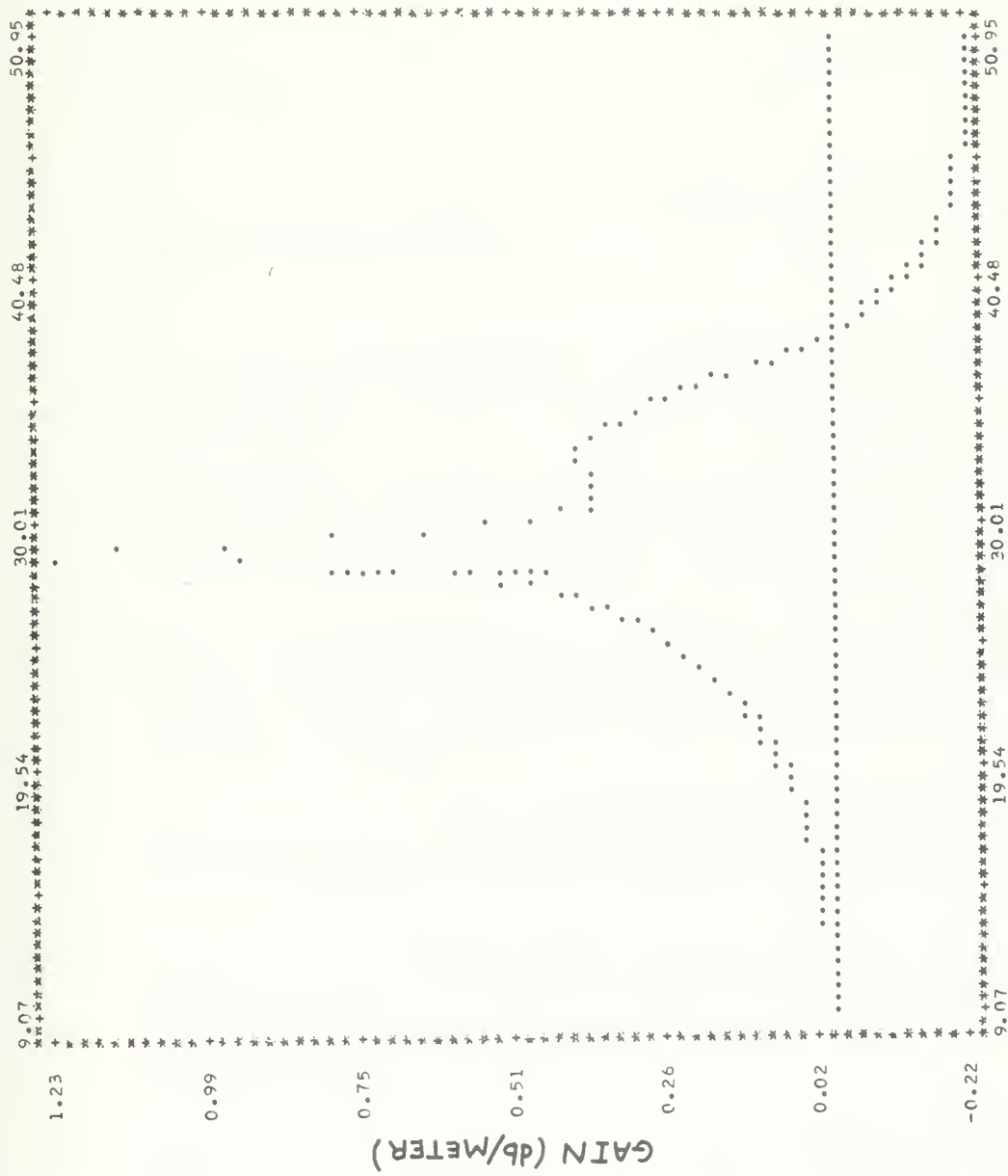
time (μ-sec.)

X-SCALE: " " = 0.523E 00 UNITS

Y-SCALE: " " = 0.142E-02 UNITS

POPULATION INVERSION BETWEEN MODES I AND II OF CO<sub>2</sub>





X-SCALE: "X"= 0.523E 00 UNITS      TIME (μ-SEC.)

Y-SCALE: "Y"= 0.241E-01 UNITS

THE LASER GAIN PRODUCED IN CO<sub>2</sub> FOR λ= 10.6 microns.



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1. ORIGINATING ACTIVITY (Corporate author) Naval Postgraduate School Monterey, California 93940		2a. REPORT SECURITY CLASSIFICATION Unclassified	
		2b. GROUP	
3. REPORT TITLE The $\text{HN}_3 + \text{CO}_2$ Laser: An Analytical and Experimental Investigation			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Master's Thesis (March 1972)			
5. AUTHOR(S) (First name, middle initial, last name) Francis Kenneth Helmsin			
6. REPORT DATE March 1972		7a. TOTAL NO. OF PAGES 79	7b. NO. OF REFS 33
8a. CONTRACT OR GRANT NO.		9a. ORIGINATOR'S REPORT NUMBER(S)	
b. PROJECT NO.			
c.		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
d.			
10. DISTRIBUTION STATEMENT Approved for public release; distribution unlimited			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Naval Postgraduate School Monterey, California 93940	
13. ABSTRACT One of the most important methods of obtaining laser action, both from a technological and scientific viewpoint, is the chemically-pumped laser. The $\text{HN}_3 + \text{CO}_2$ chemical laser has been modeled and an experimental investigation conducted to determine the existence of laser action. The analytical model has been used to predict the expected population inversion and laser gain for a range of pressures and various additives. The experimental investigation conducted for comparison with the model did not result in laser action. The increase in pressure for the mixtures investigated indicates the occurrence of an explosion. The lack of detection of laser action has been attributed to difficulties with alignment of the optical system and to signal noise associated with the flash circuit.			





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## KEY WORDS

## LINK A

## LINK B

## LINK C

ROLE

WT

ROLE

WT

ROLE

WT

Laser

Laser Gain

Explosive

Hydrogen Azide

Flash Photolysis

Chemical Laser







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